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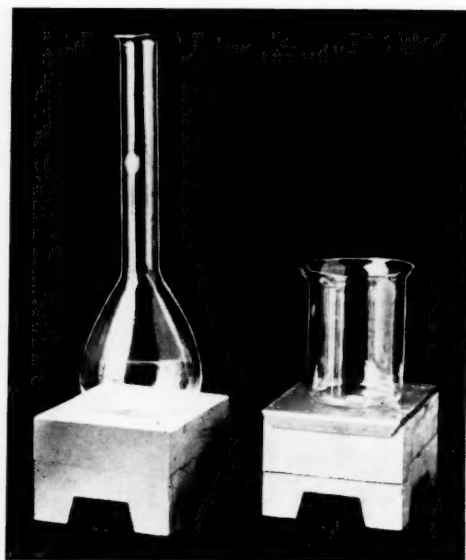
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Flour Facts---Properties That Effect Baking Efficiency

Dr. Frederick L. Dunlap of the Industrial Appliance Co.

It is an accepted fact that, only after flour has attained certain properties which it does not possess when fresh-milled, is it capable of rendering its full baking value.

Wolfgang Ostwald, in an article entitled: "Contributions to Colloidal Chemistry of Bread," says: "Wheat flours reach their full baking value only after months of storage."

Prof. John C. Summer, addressing the third annual convention of the North Dakota Association of the Baking Industry at Fargo on Feb. 2, 1921, emphasized the aging of flour through storage: "It is often the case that little thought is given to the storage of raw materials. All ingredients should be stored under as near ideal conditions as it is possible to have. Flour should be placed in a light, airy, dry room, free from all foreign odors, with a temperature of 65 to 70 degrees maintained at all times. At a lower temperature flour will age very slowly, while at a much higher temperature deterioration will quickly commence. During proper aging the gluten is matured and the flour bleached."

While there is a unanimity of opinion as to the necessity of conditioning flour before using and as to the character of storage for its proper development, owing to the complex nature of flour, rendering its analysis difficult, there is not the same widely disseminated unanimity of opinion as to what the changes are that are responsible for the improved baking value of aged flour.

FLOUR CONDITION FACTORS

As flour conditions there are two outstanding factors. It becomes whiter and its acidity increases. The intenser yellow color in fresh-milled flour is due to a chemical substance known as carotin. It is widespread in the vegetable kingdom and is taken

up by the animal in its food and appears in certain animal products such as the milk of the cow and the yolk of the egg. It is a crystalline substance closely related to a group of compounds known as terpenes. Like the terpenes it is chemically very reactive with various substances such as oxygen, iodine, bromine and chlorine. It is probable that the whitening of flour through aging is due to the action of the oxygen in the air on the carotin. Examination of aged flour reveals the fact that the outer portion in the package—that which is most accessible to the air—is whiter than the flour in the center of the package from which the air has been excluded.

For many years the examination of flour for acidity has become a routine laboratory matter. Acidity is always returned in terms of lactic acid. This is a mere chemical fiction for the acidity of flour is not due to lactic acid. "In a normal sound flour the greater part of the acidity value is due to phosphates normally present in the flour and the rest of the acidity is mostly, if not all, due to amino compounds also normally present in the flour. The phosphates and the amino compounds occur to the smallest extent in the interior of the wheat kernel and to a larger extent in the outer portions and in the bran." (C. O. Swanson).

ACIDITY OF FLOUR

In an article by Bailey & Collatz: "Study of Wheat Flour Grades," the authors say: "From the available data we conclude that the electrolytes of the water extract of wheat flours are chiefly phosphates which are produced as the result of hydrolysis of phytin by the phytase in the natural tissues of the wheat." In simpler terms, this means that in extracting wheat flour with water, a substance

(enzyme) known as phytase breaks down the phosphorus bearing substance phytin, water entering into the reaction, with the production of phosphates, which have the power to conduct the electric current (electrolytes). The acidity of a flour has been shown by Bailey & Collatz to vary with the conditions under which the water extraction of the flour is made.

From all this, it is to be concluded that the acidity in normal flour is due to phosphates and amino acids, the greater part due to the phosphates. In reality these phosphates are so-called acid phosphates, i. e., they are phosphates having an acid character.

It has been mentioned above that aging flour increases its total acidity. This increase in acidity is therefore not unlikely due, in part at least, to the slow conversion of the phytin of the flour by the phytase, and hence a gradual increase in the amount of acid phosphates present in the flour.

BAKING QUALITY OF FLOUR

Very few subjects have been under as close study as that of the baking quality of flour. Why does one flour give better baking results than another? Why does the aging of flour greatly increase its baking value? These are questions of more than theoretical interest, knit as they are with the most fundamental of all foodstuffs. It is not the intention to burden the reader with a historical review of all the researches which have been carried on, or to enumerate the numerous theories which have been advanced. It is rather to give prominence to a research carried out in 1911 in Copenhagen, a research which announced a fundamental principle with respect to the baking quality of flour. This principle has not until the past few years come into its own. One reason for this has been, perhaps, the comparative inaccessibility of the original article to

chemists in general, chemist in particular situated as they frequently are, without access to the great scientific libraries. However, this fundamental principle is now beginning to receive its just place and, through the use of modern electrical equipment in the chemical laboratory, its basic value is becoming more and more recognized.

In 1911, H. Jessen-Hansen published in the *Comptes Rendus des Travaux du Laboratoire de Carlsberg* an article entitled: "Studies on Wheat Flour. Influence of the Concentration of Hydrogen Ions on the Baking Value of Flour." Let us take a moment to see what these hydrogen ions are. We all know in a general way what acids are. They taste sour and turn blue litmus to a red color. All acids (as well as so-called acid salts) contain the element hydrogen. Chemists recognize weak acids and strong acids. Wherein do these differ? We are now speaking of these acids when mixed with water. All acids, in water solution break down or dissociate into hydrogen and whatever else the residue attached to the hydrogen may have been. This dissociated hydrogen is not the hydrogen which we recognize as an element. Elemental hydrogen is a gas. The dissociated hydrogen differs in that it bears a positive charge of electricity. Now the undissociated acids in a pure state, when mixed with water dissociate to different degrees. The positively charged hydrogen is known as an "ion". It is found that under comparable conditions an acid like acetic acid—the acid of vinegar—dissociates to form a relatively small amount of these hydrogen ions, while muriatic acid (hydrochloric) dissociates very greatly and sulphuric acid somewhere between these two. Hydrochloric acid is therefore spoken of as a strong acid and acetic acid as a weak one. All of this leads to another yet simpler mode of expres-

sion; we may speak of the "intensity" of an acid, thereby implying the hydrogen ion concentration. "Intensity" must not be confused with "acidity" from a quantitative standpoint. Several solutions may have the same quantitative degree of "acidity" but varying greatly in their "intensity." The intensity factor is coupled solely with the concentration of the hydrogen ions and this varies with different acids, under comparable conditions.

INTENSITY OF ACIDITY

An admirable example of the difference between the acidity of flour and the intensity of such acidity has been brought out by Jessen-Hansen. It has been pointed out above that the phosphates and amino compounds occur to the smallest extent in the interior of the wheat kernel and increase in the outer portions. From this, we should expect our highest grade flours to contain the smallest quantity of acid. This is experimentally found to be true. The lower grade flours, containing as they do, more of the outer portions of the wheat kernel, would be expected to contain the higher amount of acidity. This has also been found to be true. However, Jessen-Hansen has experimentally determined that the intensity of this acidity is the reverse of the quantity of acidity; that is, the intensity of the acidity of the highest grade flours is greater than that of the lower grades from the same wheat, although the quantity of acidity is less.

What Jessen-Hansen has done, in the article referred to, is to study the effect of this intensity factor of acids in the baking value of flour. His work was carried on with a scrupulousness of detail which led him to most convincing conclusions. It is these conclusions that are fundamental in our knowledge of the baking value of flour and they are now receiving verification in the hands of

other researchers. Why the intensity factor of acids is so fundamentally important has also been the subject of convincing research, but more of this phase later.

CONCENTRATION OF HYDROGEN IONS

In his resume, Jessen-Hansen says: "For the dough of any wheat flour, there exists a determined concentration of hydrogen ions, with which the production of bread from this flour will be the most successful, and this concentration is greater than that which is found in a dough made from the flour in question freshly milled."

* * *

"This optimum corresponds approximately to the exponent of the hydrogen ions $\text{pH} = 5$."

For our purpose, we need not worry ourselves as to the exact meaning of this $\text{pH} = 5$, except to realize that it is an exact quantitative measure of the intensity factor mentioned above.

From Jessen-Hansen's work then, there is this important conclusion, that in order to get any flour to give its highest baking value the intensity of its acidity must be at the proper point.

With these views in mind, the increase in the baking value of flour through aging becomes intelligible, for as Jessen-Hansen points out: "In view of these facts, the results at which we have arrived have suggested the idea that the essential effects in the storage of flour consist in an increase in the acidity, which approaches the state where it would give to the dough the optimum ionic concentration, a state which the flour attains but even exceeds. However, this conclusion is not in the least premature. In fact, among the experiments, the results of which are given in Table II is one which militates in its favor."

From the above we can definitely conclude that flour, as it ages, becoming as it does increasingly more acid in quantity, also increases in the in-

tensity of this acidity until it reaches a point where it causes the flour to give its highest baking efficiency. Beyond that optimum point, storage acts adversely, that is, the baking efficiency begins to lag. Flours which are very acid do not bake at all well, but if mixed with fresh flour, the mixture gives better results. This merely means an adjustment of the intensity of the acidity toward the optimum point, by mixing a flour (old) with too much intensity of acidity, with one having too little (new).

There is yet another important conclusion, which Jessen-Hansen has drawn:

"The different artificial means preached in recent times as being capable of ameliorating flour, none are of value other than that of increasing the hydrogen ion concentration in dough." This means that of the methods in use or recommended, to dispense with aging and to give, through some treatment, to the freshly milled flour its highest baking value, the only ones of value are those which are capable of modifying the intensity factor of the acidity to the optimum point.

Such methods have their place in the great milling industry provided they are from all standpoints unobjectionable. As Ostwald states in his article above referred to, "It is evident that the acceleration of the aging process is of great economic importance, for upon it depends the yield of the dough and of the bread."

PHYSICAL PROPERTIES OF FLOUR

The next question needing an answer is, "How does this intensity factor affect the physical properties of flour so that the baking qualities are so much enhanced?" The answer revolves around the physico-chemical properties of the gluten.

In a report of their experiments on the "Influence of Electrolytes Upon the Viscosity of Dough," Henderson, Fenn and Cohn point out that "the

rising of bread and the quality of the baked loaf depend upon the nature of the dough and especially upon such of its properties as tenacity, ductility, and elasticity. These properties are hard to define theoretically in this complex colloidal system, but they are, as we have found, related to viscosity or to whatever may determine the resistance of dough to stirring and to flowing through a tube. It is evident that with the variation in hydrogen ion concentration, viscosity passes through a minimum a little on the acid side of $\text{pH} = 5$. Jessen-Hansen has found $\text{pH} = 5$ to be the best hydrogen ion concentration in bread making and it is also, as we have observed, the most favorable reaction for the rising of dough. Observations of our own (except with a very weak flour) agree with those of Jessen-Hansen. We have also made numerous measurements of the hydrogen ion concentration of bread procured in the market, which are entirely consistent with this view. Our studies, reported in another paper of the rising of dough and the carbonic acid production during fermentation indicated that the best results are obtained near the point of minimum viscosity."

Here is a splendid confirmation of the work of Jessen-Hansen and of the intimate and fundamental relationship of the intensity factor of the acidity to the production of highest baking efficiency in flour. The further point is developed that the effect of this intensity factor is on the viscosity of the dough and that the minimum viscosity of dough is near this $\text{pH} = 5$ which Jessen-Hansen found was the best for producing the finest results from any flour.

EFFECTS OF ACIDS ON GLUTEN

The next step in an understanding of this interesting subject is to relate briefly some of the studies that have been made on the effect of acids on gluten. Wood, and Wood and Hardy

have shown that gluten is what the chemists call an "emulsoid colloid" and that its properties are much modified when placed in varying concentrations of acids and salts. Small bits of gluten, which had been washed out from wheat flour, were suspended over glass rods and immersed in solutions of varying concentrations of acids and salts, or mixtures of the two. A study was then made of the effect of the different solutions on the disintegration or loss of cohesiveness of the gluten. A very curious phenomenon is noticed as the concentration of the acid was increased. When the gluten was suspended in distilled water its cohesion was retained almost indefinitely. When immersed in an extremely dilute hydrochloric acid (0.00365%) the gluten almost immediately began to lose its cohesion, i. e., it began to "disperse" in the liquid medium. As the concentration of the acid was increased this action increased up to about a 0.122 per cent of acid. From this point, as the concentration was increased still further, the dispersion began to decrease and at 0.304 per cent the gluten became "permanently coherent and much harder and more elastic, and less sticky than its original condition."

All this is extremely important from a practical as well as a scientific viewpoint, for it shows how the physical properties of gluten are subject to extreme modifications by variations in the concentrations of hydrochloric acid, that is to say, by a change in the intensity factor.

SWELLING OF WHEAT GLUTEN

Some years after Wood and Hardy's work appeared, Calvin and Upson published an article "On the Colloidal Swelling of Wheat Gluten." They say: "It was already known that proteins, to which group of highly complex chemical substances gluten belongs—would swell in dilute acid solutions." Small disks of wheat

gluten were cut from material washed out from wheat flour and weighed, after which they were immersed in various strengths of solutions and their physical change noted even to their change in weight. For our purpose the interesting thing to note is the fact that in increasing concentrations of various acids the gluten swelled more and more and took to itself water from the solution (hydration). This increased up to a maximum point, and then the swelling and hydration began to decrease. This maximum point was not the same for all acids, but this is not to be wondered at. Here again we see the extreme susceptibility of gluten to modify its physical character by acids of varying concentration, i. e., of a varying intensity factor.

Perhaps the most extensive and profound study of this subject has been made by Ostwald and Luers. In various articles published during 1919 and 1920, they have outlined all of their observations and deductions under the general caption, "Contribution to Colloid Chemistry of Bread." It is impossible, within the scope of a brief discussion such as this, to give any adequate outline of their experiments. They not only substantiated the work of Wood, Hardy, Calvin and Upson, but went into still greater detail in their study of the modification of the physical properties of gluten, not only through acids, but various salts as well.

Ostwald has described the value of proper viscosity of dough on the character of the bread produced: "The dough must possess a certain average viscosity or solidity in order that a given volume of gas will form as many small pores as possible. From the point of view of the mechanics of liquids, the dough must exhibit great viscosity. If it were too fluid, then the bubbles of gas would quickly flow together to form larger volumes, and this is well known to be

a bad defect in baking. On the other hand, the viscosity of the dough must not become too great; the dough must not be too "short." Then it would be too viscous and, consequently, its physical behavior during the short period of baking would be more like that of a solid body. The bread frame (erumb) would solidify too rapidly and break under the pressure of escaping gases. In this case also, would be produced a final defect in baking, namely, the formation of large hollow spaces. From the point of view of mechanics of solids, dough must possess a great resistance to wear and tear and at the same time have considerable elasticity or ability to change form. This plasticity is not identical with the term elasticity which latter term means automatic returning to the original shape after a previous change, although, naturally great elasticity presumes great plasticity, both qualities being closely related."

In order to connect this subject matter of the quotation from Ostwald, given immediately above, it is only necessary to mention what Luers says with regard to it: "* * * It is plain that all conditions which would affect the condition of the gluten must also affect the baking quality and the phenomena which take place during the process of baking. To these phenomena particularly belongs the swelling of the gluten proteins and of the gliadin especially." In this connection it is necessary to mention that wheat gluten is made up of two different compounds or proteins—glutenin and gliadin.

Luers again states: "It is known in the baking practice that gluten exhibits an increased swelling under the effect of acid, it becomes softer and more capable of being stretched. * * * Still, the acid can have unfavorable effects * * * when the actual acidity or hydrogen ion con-

centration is especially high, as is frequently the case with old and long stored flours, or from flours from germinated grains." Here we have pointed out the evil effects of too high an acid intensity factor, as in excessively aged flour. These bad effects are possibly for the most part due to an unfavorable physical condition produced in the gluten. Luers in discussing this point further says: "It looks as if a certain concentration of hydrogen ions is most favorable for the swelling phenomena of gluten, and consequently, also for the baking quality of flour. We are spared of experiment in reference to this point, for Jessen-Hansen already has treated the question in a very extensive and exhaustive way. * * * Since this $\text{pH} = 5$ is very important for the baking process, all conditions which tend to this hydrogen ion concentration deserves consideration."

It is not desired to imply that the intensity factor for the acidity of a flour is the sole determining factor in ascertaining the baking quality of flour, yet it is probably the most important factor. As Cohn and Henderson have pointed out: "In sum, the acidity of the dough at the time of baking seems to be the most important variable factor in bread making." These authors are of course, referring to the intensity factor of the acidity rather than to that of the total acidity present.

CONTROL OF ROPE

It has been known for some time that by adding acids to dough that "rope" could be controlled. Quite a little work has been done in studying the intensity factor of this acidity, to control the development of "rope." It is of more than passing interest to note that the intensity of acidity found by Jessen-Hansen to give the best baking quality to a flour is also the one necessary to control rope. Cohn, Walbach, Henderson and Catheart in discussing this

point, say: "As a result of this investigation it seems clear that, when possible, the hydrogen ion concentration of bread should be maintained near $\text{pH} = 5$. Our observation on rony bread, both in the laboratory and in the bakery, seems to indicate that such practice would prevent the occurrence of rope."

VALUE OF ANALYTICAL FIGURES

Much stress has been laid in some quarters on the results obtained from the chemical analysis of certain ingredients of flour and their interpretation in terms of baking quality. It is certainly a moot question just what value these analytical figures are in this regard and surely there can be no hesitation in accepting a result obtained solely from submitting flours to the oven test. After all is said and done, the final answer to a flour's baking value is told in the bake shop. On this point it is interesting to note a few observations of workers in the scientific field of flour. Ostwald remarks: "Although the baking qualities of the flour undoubtedly plays a main role in the preparation of bread, yet it is the unanimous decision of practical men that there still is no method by which this quality could quantitatively be determined in a laboratory. All figures obtained by physical, chemical and technical procedures and referring to the baking qualities of flour have proved to be unreliable and ambiguous. Among others, M. P. Neumann emphasizes the fact that the baking quality at the present time can only be judged by results of a baking experiment."

Now much stress has and is being laid on the washing out of gluten from flour as an aid in determining flour quality. Jessen-Hansen did much work on this subject and concludes that "The extraction of gluten by washing should be definitely and irrevocably considered as being without value in so far as the analy-

tical method serves to determine the industrial value of a wheat flour."

Luers says: "The method of washing out gluten is unsufficient for analytical purposes. In summing up all these facts we have come to the same conclusion as did Jessen-Hassen from his experiments, namely, that the washing out of gluten is useless as an analytical method. The amount of gluten greatly depends upon the prevailing reaction of the medium and upon external influences. Even at small concentrations of acids, so small that they did not correspond to the optimum concentration required for the baking quality, the washing out of gluten becomes impossible; the same applies to yeast doughs after completed fermentation, in which case the washing out of gluten is hindered by the swelling, which in turn is due to carbonic acid. On the other side, at such degrees of acidity at which normally no gluten can be washed out, the possibility of washing it out can be reestablished when there is present a great quantity of neutral salts which act against the swelling effects of the acid. Even in the neighborhood of the neutral point the neutral salts can cause such shrinkage of gluten and to such a decrease of its solubility that the result would be formation of a crumbly gluten falls to pieces."

All of this is extremely vital to the miller and the baker. The valuation of the baking quality of flour through analytical procedure is open to serious doubt. There neither is nor can be any question, when the answer given is by properly conducted baking experiments.

Mention should be made of some experimental work on gluten by Calvin and Upson. In commenting on their work, Luers says: "Finally, the American investigators have submitted to extensive criticism and testing the method of washing out the gluten, and their results agree in all es-

sential points with the views expressed by us. However, we agree with Jessen-Hansen that the method of washing out the gluten is to be rejected in reference to drawing any conclusions based on the amounts of washed out gluten, while Upson and Calvin, on basis of their experimental researches and theoretical considerations, propose a standard method, in which the chief consideration is to do the washing out with freshly distilled water. Still, as pointed out, the American investigators, too, put the main stress on the quality of the washed out gluten in opposition to the quantity. The proposed standard method will, consequently, render good service, if the qualities of gluten will furnish an insight into the baking quality of the flour under consideration."

There has been given a brief epitome of certain important scientific work bearing on the reasons for the improvement of flour by age. It is sufficiently clear that it all seems to center about the increase in the intensity of the acidity. We know, further, that the aging of flour is by no means a commercial practice, as highly desirable as such a practice may be. The reason is not far to seek. It is a financial question primarily. "It is evident that the acceleration of the aging process is of great economic importance, for upon it depends the yield of the dough and of the bread." (Ostwald). The increase in the intensity factor of the acidity of freshly milled flour can be and is accomplished now in the mill without the necessity of storage.

CONCLUSIONS

1. A freshly milled flour is not in condition to render its highest baking value. On storage such a flour increases in acidity and whiteness. It also increases in baking quality until it reaches an optimum, after which it begins to deteriorate.

2. Jessen-Hansen and others have

shown that the optimum baking quality of every flour is developed for the particular purpose for which its inherent properties render it suited, by having the intensity of acidity at a certain point. This intensity point differs only slightly in different flours.

3. Investigators have shown that this intensity of acidity exercises its good effects on the baking quality of a flour through the gluten, whereby the latter has its physical properties favorably affected.

4. The storage of flour, therefore, benefits it through the natural increase in the intensity of its acidity. When this has reached the optimum point, the flour is then ready to render its utmost in the oven. Further storage develops an excessive intensity of acidity and this acts in a detrimental fashion.

5. Storage of flour for the increase in baking efficiency is commercially unfeasible and not generally practiced for obvious reasons.

6. The lack of definite knowledge heretofore, of the cause for the greater baking efficiency of aged flour has led to numerous suggestions in literature and art for the improvement of the baking value of flour. Some of these only artificially whiten. Others add in small or minute quantities solid substance in powdered form, and still others apply substances in the form of vapor for more uniform distribution. Jessen-Hansen says of these: "None are of value other than that of increasing the hydrogen ion concentration (that is, intensity of acidity) in the dough."

7. Any method which can duplicate the results of natural storage on flour, if at a reasonable cost and free from all objections, is a marked benefit to millers and also to the flour-consuming public.

Comptes Rendus des Travaux du Laboratoire de Carlsberg, Vol. 10, P. 170
(1911)

STUDIES ON WHEAT FLOUR

Influence of the concentration of hydrogen ions (1) on the baking value of flour

H. Jessen-Hansen

Editor's Note:—It is to be regretted that I am unable to furnish the charts and tables for this most instructive paper; but believe that the body of the paper warrants its publication.

INTRODUCTION

During the course of a series of experiments, over several years, to which I have occasionally devoted myself, with the view of finding the correlation existing between the chemical composition of a certain wheat flour and the baking value of this same flour, I have noticed a fact, until now unobserved, and which is not without importance for the solution of the so much debated question, and which is not without presenting interesting points of view in the practice of baking. That is why I wish to give a summary of results, at which I have arrived, up to the present time.

If one makes bread, following all the rules of the art, with wheat flour making the dough with distilled water containing salt, and yeast, in proper proportions, it has been verified that if one adds any acid whatsoever to the water, the specific gravity of the bread undergoes a sensible modification, in the sense that it diminishes when the amount of acid is increased to a certain limit, but to increase it again, one has to add acid up to the point where the taste of the bread is sour.

It has been verified that the addition of the acid not only influences the specific gravity of the bread, but its quality in general, in such manner only by a determined but small

quantity of acid, able to develop the properties, which taken in all, in practice is called the baking value of the flour—such as the form, the exterior and interior color and the quality of its porosity. In other terms, it has been established that there exists an optimum concentration of hydrogen ions, for baking value in general, or in all cases for almost all of the diverse properties which one constantly understands under this designation. The yield, on the contrary, *does not appear to be affected by the addition of acid.* (1) For the significance of this term, see S. P. L. Sorenson, Enzyme Studies.

These verifications made, the first problem to resolve, would be to determine that optional ionic concentration and to learn if it would be always the same whatever the quality of the flour.

In principle, the manner of proceeding with the solution of this problem is very simple. One has only to make a series of bakings of bread, by adding to the water before it is used in making the dough, different quantities of any acid whatsoever and measuring the hydrogen ion concentration of the dough thus prepared. For the rest, one has merely to treat it and bake it according to the rules of the art, then to determine the specific gravity of the loaf, to compare then the different values pertaining to any two quantities, or it may be put together in a synoptical table. What is better, is constructing a curve of which the

(1) See S. P. L. Sorensen, previously cited.

abscissa represents the index of the hydrogen ion concentration (1) and the ordinant the the specific gravity or better the specific volume (2), for it is this last which constitutes the most direct expression of the baking value of flour.

In this last case, the abscissa of the peak of the curve indicates the optimum concentration of hydrogen ions, that is to say, the concentration at which the flour under consideration possesses the greatest baking value. In repeating the operations on other flour samples we then obtain, if the ionic concentration is the sole determining factor, curves coinciding with those constructed in the first case, making allowance for experimental errors, while the existence of other factors reveal themselves by different configuration of the curve, represented by different flours.

However, if the principle of the research is simple, its execution has difficulties. At first the preparation of bread is an operation complex enough during the course of which a number of factors enter into play and hamper the results, such as the practice of the baker, diverse circumstances of a psychological order, the quality of the yeast, and still others. On the other hand, the determination of the hydrogen ion concentration is not a simple matter. We shall return to this point later.

A. EXPERIMENTAL METHODS

1. Manner of carrying on the baking.

In that which concerns the preliminaries in the baking of bread, we have endeavored, as much as possible, to eliminate the uncontrollable factors, or to limit their influence.

First, it was a skillful baker, knowing the practice of his trade, who carried on the baking experiments in

the laboratory, under my direction and constant surveillance.

In the second place, we have, as far as possible, carried out the same day and with the same leaven, all the experiments which were to be directly compared. As we have been even able to make five experiments in one day, it follows that the experiments of one day suffice to construct the curve mentioned above, provided one has carefully chosen convenient differences in the ionic concentration.

In the third place, we have repeated the experiments three or more times on different days to take in consequence, the mean of the results as a definite expression of the specific volume for the ionic concentration in question.

In the fourth place, I have not put the baker in touch with the result which I have obtained from each experiment after it has been terminated. Also, in repeating a series of experiments I have, without his knowledge, varied the order.

Finally, we have always, as near as possible, employed leaven of the same age and quality. The leaven used was the aerated yeast (1' aeroleuvre) which the distillery and yeast factory "Fortuna" obligingly placed at my service. I wish to thank here again, the factory director, Mr. P. J. Thomsen, for the courtesies which he has shown me under these circumstances. We brought the yeast each day from the factory immediately after it had been pressed, and usually it was made use of the same day. It is only in the last series of experiments that for diverse reasons, it was more convenient to bring the leaven the eve of its use and to preserve it meantime in a refrigerator. It does not appear, however, that the results are affected in any fashion.

One might perhaps object and that I should have employed a sure yeast culture prepared in the laboratory, for the baking to be more sure al-

(1) See S. P. L. Sorenson, previously cited.

(2) That is to say, the volume, expressed in cubic centimeters, of one gram of bread.

ways of operating with identical material. I believe, however, that the procedure I have followed has given the greatest guarantee in this respect; for the identity of the leaven evidently does not consist solely in the unaltered purity of the race, but it is also of importance, and perhaps even of greater advantages that its physiological condition in general, remains the same. In all cases, in the product of the laboratory, where one works with only small quantities and where, in consequence, chance comes to play an important role, it appears to me there are fewer chances that this latter condition would be affected, when produced on a large factory scale, where one of the principal conditions and one of the commercially advantageous results is precisely that the merchandise be constantly uniform as possible, and where, in consequence, it is important that scientific experience be employed to bring about that uniformity. Be that as it may, the results that I have obtained, do not cause me to regret my choice, although from time to time, phenomena were observed, in default of other explanation, we have believed were placeable to the account of the leaven.

The following is the mode of operation which we have followed in our bread baking experiments:

For each experiment we took:

1—About 1100 grams wheat flour, a little more or less according to the quality of the flour, and which was weighed with a precision of 2 grams (The limits of error indicated are of the maximum values.)

2—Salt, 5 grams (25 mgr.)

3—Leaven, 15 grams (25 mgr.) and

4—Liquid 650 cc. (2 cc.)

One prepared all at one time a quantity of liquid such as is sufficient for all the experiments which

it is the intention to make with a liquid of this concentration.

To begin with, one weighs out a little more (about 100 gms.) of flour, which is not to be used in the experiment. Note the weight, then provisionally put to one side a small portion, say 1-6 — 1-7. Measure the temperature of the flour and sprinkle the salt over the main portion. The liquid was then heated to a temperature such that added to that of the flour, reached 49 degrees, experience having shown that the dough finished thus obtains the desired temperature, 25 degrees. Then I measured 650 cc. to send back that portion to the baker who after having diluted the yeast, makes the dough with the principal portion of the flour and just as much of the smaller portion as he may judge necessary to give to the dough a suitable consistency. One measures the temperature of the dough obtained; it does not deviate 1 degree from the 25 degrees, and in the majority of cases it does not deviate at all. One places the dough then in a fermentation box, of which the temperature was maintained, by the aid of electric lights, as nearly as possible at 30 degrees. (In our last experiments we have used as a fermentation box a Rohrbey water bath, in which the thermometer, plunged into the water was maintained at 32 degrees.) Next, to prevent a too great drying of the surface, place at the side of the dough a receptacle containing some water.

After leaving this for an hour, knead the dough for the first time, and after leaving it half hour more in the fermentation box, subject it to a new working. I immediately after make the dough into four loaves of equal size, which one puts into some moulds made of tin plate. One replaces these in the water-bath, in order to make the bread rise for the last time, a process which one inter-

rupts when the moment has arrived in which the baker judges the bread is ready. The duration of the last fermentation was found to be different for the different kinds of flour, to make it exact, this matter was left entirely to the judgement of the baker.

In kneading and forming the loaves, one used the small portion of flour that was set aside in the beginning of the experiment, while that which remained after the bread had been put into the moulds was weighed and deducted from the quantity weighed originally. The difference was then the weight of the flour which had served to make the bread and which was the base upon which one calculated the yields. In order to be very sure that, in appraising the dough, the baker depended each time upon his own personal estimate of the actual state, without having regard for the quantities of flour employed in the other experiments, he was always left in ignorance of how much flour had been weighed, a quantity which was varied within limits sufficiently narrow. But, I am able to state that the errors between the quantities which he used in repeating the same experiment were generally slight enough, and I estimate that even the more remote results will give in some sort of measure of the degree of the pre-precision with which we have worked.

The baking of the bread made in an experimental oven tested out by Christy Bros. & Co., of Chelmsford. The oven was electrically heated by 5 heating elements composed of spiral resistance wires, of which three are found on the bottom of the oven, under the grating upon which the moulds are placed. The two others are placed in the upper portion. Care is taken that at the moment the baking is started, the thermometer fixed in the oven door registers 230

degrees and that this temperature is maintained as closely as possible while the bread is in the oven, that is to say, for a half hour (1). When this time has passed, the bread is removed from the oven and let cool until the next day. It is only then that it is weighed and its specific gravity determined.

This determination was effected in the following way: a box or sometimes a cylindrical glass with thick walls and of convenient size was filled to the top with peas which have been well settled in place. After this remove a portion in order to place the bread in the box. Fill again with peas which are settled down carefully in the first case, by tapping the box. After this square off the surface and weigh the peas thus replaced. Their weight gives a measure of the volume of the bread, when one has knowledge of the measure of the capacity in dividing it by the weight of 1 liter of peas (in this particular case 864 grams.)

The method just described might at first seem somewhat primitive, but repeated attempts have convinced me that with the requisite care it is sufficiently accurate. Two determinations, made in this manner, of the specific gravity of the same bread never differ between themselves over 1% at the outside. As in the other determinations relative to the baking of bread, one could hardly count on greater precision, I think that it is entirely sufficient and there is no need to have recourse to methods more exact and at the same time more complicated, even if such were available.

As we have in each experiment baked four loaves and the experiments repeated usually three times,

(1) Upon the grating is placed, besides the moulds, a flask containing boiling water, so as to approach as nearly as possible, conditions existing in an ordinary oven, where steam is always made to pass during baking.

it follows that the values given for the specific volume in the following, represents the mean specific volume of twelve loaves.

2. DETERMINATION OF THE HYDROGEN ION CONCENTRATION.

If we now look at the other side of the question, the determination of the concentration of the hydrogen ions of the dough, it is at first necessary to note that it is impossible in any way to calculate it from the amount of acid added for it is practically neutralized by the basic constituents of the flour. One does not gain any advantage by titration, seeing that any method of titration does not inform us on the point which alone is of interest in this case, namely, knowing the concentration of the hydrogen ions possessed by the solution at the moment titration is begun. The titration determines only the amount of acid or base required to change the unknown ionic concentration existing at the beginning of the titration in such a manner as to make it coincide with that which determines the end of the titration and which corresponds to the end point of the chosen indicator (1). Moreover, so far as I know, there exists no method for the direct measurement of the hydrogen ion concentration in dough.

Also, happily this is not necessary. One can content himself with merely determining the ionic concentration of a dough "diluted" in the definite proposition with aid of one or the other of two methods set forth by S. P. L. Sorensen (2), to determine by colorimetry or electrometric methods, and then admitting that by this determination one arrives at the time concentration of the hydrogen ions in the dough, multiplied by an unknown factor, it is true, but which depends only on the dilution and

consequently, one is able to leave out of consideration the condition of always operating under the same dilution. Consequently, the process employed has been the following:

Of the liquid used in the baking experiment in question, measure the quantity which under the conditions for preparing the dough is necessary to make a dough with 25 grams of flour. Dilute this amount in a flask up to 100 cc. with boiled distilled water. Place 25 grams of flour in a 150 cc. Erlenmeyer flask. The two flasks were corked and placed in an ice box 'till next morning. Then pour the liquid on the flour (1) and agitate strongly; taking care to get rid of the lumps formed. Place the mixture for two hours in the ice-box, shaking frequently. In the magma thus obtained, determine the hydrogen ion concentration by the electrometric method and without filtration, either by the method of S. P. L. Sorensen, or by the later method of K. A. Hasselbalch (2.) Sometimes the ionic concentration was determined in the filtered liquid by the electrometric method and sometimes by the colorimetric, using p-nitrophenol or methyl red (3) for an indicator.

The electrometric method shows the same results on the filtered as on the unfiltered liquid. As to the colorimetric measure, they agree well with those in which samples contained but small quantities of acid. While the agreement is less good in the case where larger amounts of acid were used, that is to say, where the exponent of the hydrogen ions ap-

(1) Being given in the dough to be baked a ratio of flour to liquid has a mean value without great variation of 1160:650 and that the ratio of flour to liquid in the "diluted" dough is constantly 1:4, it follows that the ionic concentration has been measured in a "diluted" dough on the proportion $4400:650=6.77$.

(1.) S. P. L. Sorensen loc. cit. P. 8.

(2.) Loc. cit.

(2) This completes Rendus 10,69 (1911).

(3) Ibid. 10,162 (1911).

proached 5, or was less than that number. This indicates surely that in this case a larger proportion of protein has entered into solution and which has for its effect the lessening of the delicacy of the indicator (4), as also it renders filtration more difficult, to the point that great pains are necessary to obtain the filtrate sufficiently clear.

B. EXPERIMENTAL RESULTS

Having examined in the manner described above 16 different flours, all relatively freshly milled, as well as 4 acids, I have verified that all flours are influenced by the addition of acid, in the manner indicated, though to different degrees. I have also established that for the same concentration of hydrogen ions, the different ions do not present sensible differences. Hydrochloric is the acid upon which the greatest number of experiments have been made, but with it, experiments have been made also in acetic, lactic and phosphoric—the last because it is a part of all flours, and with lactic acid, because it is said to be found in old flour.

The results at which I have arrived are found contained in table I—III and the diagram I—III show these results graphically.

Table I and diagram I shows the experiment made on a type of flour known in the trade as 70% (called in America "Straight.") In all these experiments only hydrochloric acid was used. The flour was prepared from 5 kinds of wheat, each of very diverse origin, and also from mixtures of these wheats.

We ought to disclaim picking out the flour furnished by each one of the wheats, not having had at our disposition any apparatus which would have permitted us to accomplish this selection in the milling of the small quantities of wheat.

The experiments recorded in the table and diagram II were carried out on samples of flour of better quality, which the milling industry could furnish and which is found in the industry under such names as for example "Patent," flour which more often represents 30% of the weight of the wheat (the percentage may sometimes attain 50%.) In these experiments we have made use of not only hydrochloric acid, but also of the three other acids named above.

Table III as well as diagram III, contrary to the preceding table, contains the experimental results carried out on the most ordinary flours which are in commerce in the country and which are sold under the name of "Flormel" etc. They constitute the residue or remainder after furnishing 30-50% of flour of the first order. Moreover we find here, under No. 15, the results of a series of experiments made with a mixture of flour used in a bakery in Copenhagen and made of two parts of flour pertaining more to this class and one part of the finest American flour (Herald.)

Concerning the contents of the diagram, the first three or four vertical columns are understandable without the others; finally to aid the understanding of the other columns, which are the most essential portions, we have given the following explanation:

As may be seen, we have united the horizontal series of numbers, in groups of four, one group for each sort of flour, in such a manner that the four numbers of the same column, relate to a single experiment. In the first series of each group, the amount of acid employed for each kilogram of flour is indicated in equivalent milligrams. The following series, embraces the exponent of the hydrogen ions pH determined in the "diluted" dough; that is to say, the values, which under the corres-

(4) S. P. L. Sorensen loc cit.

ponding diagram is carried the abscissa. In the third series are the specific volumes observed in the bread; that is the volume of 1 gram of bread in cubic centimeters or that of one kilogram of bread in liters; in the diagram these numbers are carried by the ordinant. The figures in heavy type of the second and third series are the optimum values observed. In the case where the values of the specific volume in the first vertical column has been put in parentheses, the experiments have not been made without the addition of acid, and these values have been taken in the series which is found above.

Finally the fourth series indicates, for the first series indicates, for the first series of experiments, the yield, that is to say, the quantity of bread obtained, in any particular experiment, for one gram of anhydrous flour. The dry material was always determined by drying the flour in vacuum at 80 degrees for 16 hours. In the last series of experiments we have given in the place of the yield a figure to characterize in a general manner the baking volume of the flour (without taking into consideration the specific volume) and designate by the term "Note" taken in the same sense as it serves to characterize the results of an examination.

In effect, for one thing, the figures in the tables, as also the results in our other experiments, establish that the yield is not influenced by the acid added (1) and, for another thing, as we have already remarked, not only the specific volume but also the other properties of the bread are favorably influenced. We have therefore, attempted, if it be possible, to give in figures this effect of the

addition of acid, by imagining a system of notes. To this end we have assigned a numerical value to those properties susceptible to an appreciation of this kind. Then we have added these values and divided by the total the "Notes," which gives a final "Note."

The properties, for which the indicated figures are destined to represent the whole, are five in number:

1 The form and exterior aspect of the bread in general (without taking color into account.)

2 The color of the crust.

3 The fineness and homogeneity of the texture or porosity.

4 The color of the crumb, and

5 The greater or less facility with which the dough may be worked (2).

Consequently we have proceeded in the following manner:

We have set perfection on all points 8 and according as we have estimated this perfection to vary more or less, we have diminished the "Note" in proportion. The four loaves of one baking were judged together and received a "Note" in common for each of the five properties named above. Inasmuch as we have generally made three bakings, it follows that the figures given in each table represent the mean of 15 special "Notes;" consequently, they are we believe, to be considered as approaching quite closely the values of the loaves in every case pertaining to a single series of experiments, and this, so much the more when all the properties are, in general, similar, and when the decrease in one of them is not compensated by an improvement

(2) Besides these enumerated properties there might still be a question of the giving of "Notes" to two others, namely, to the odor and the taste of the bread, but the differences noticed have been so small that we have believed it unnecessary to take them into account. Be that as it may, we are disposed to think that these at their optimum coincide with that of the specific volume. In any case, its value is not diminished and it has not been observed, in so far as the acid is concerned, that it has objectional effects in other ways.

(1) Often a series makes an exception as in No. 1 of table II, when it appears that a regular influence is being manifested; however, it is not capable of being repeated, hence should be regarded as accidental.

in another. That is why it appears to me just to give the "Note" with two decimals, although at first sight it would appear somewhat bold.

On the contrary, in the comparison of values of different series, it is advisable to be more prudent—in this regard as moreover in others in considering that these values do not relate to the "Notes" given simultaneously. It is the comparison of the loaves made with the same flour which presents the greatest interest.

As the application of this system improves only with time, we have given these results only in the last series of experiments; as to the others, the first series would surely give similar results, in accord with the fact that it was they, which induced us to make the experiment of a system of "Notes."

If now we pass to a deeper examination of the tables and diagrams, a glance at them—especially of the last ones—will convince us of their accuracy, of which we spoke in the introduction, and to know that *for each of the flours examined there is an optimum concentration of hydrogen ions, which determines the largest specific volume*, and which optimum is obtained only after the addition of a more or less large amount of acid. The diagrams demonstrate at the same time that *this optimum also applies to those diverse properties characterized by the "Note,"* and that it follows, in a general fashion, a parallel to that of the specific gravity.

We are therefore dealing with a general law, so much the more as the diagrams include all the experiments made, except some preliminary experiments in which I had to grope about in order to find the convenient amount of acid to use. Moreover, these preliminary experiments militate in favor of the rule we have established. The single exception we have encountered is No. 7 in table

I (mixture of flour, in experiment in fourth column $\text{pH} = 4.90$) but in reality this apparent exception is not really one, because due to accidental circumstances the experiment in question was not made at the same time as the others of the series, but in a day apart, which in reality renders a comparison illusory. That is why the relative figures in this experiment have been put in parenthesis and is not taken into account in constructing the corresponding curve.

We see, at the offset, that this optimum, although there is some slight difference for different flours, *is found in all cases in the neighborhood where the hydrogen ion has an exponent of pH for better grade of flour*, while for the ordinary varieties this value seems to be a little higher.

As to the relationship existing between the ionic concentration of the real dough and the "diluted" dough, it appears to me that it would be greater in the former, without, however, showing any sensible difference. Be that as it may, we might say that the real dough has been diluted in the proportion 6.5:44 (which has been previously discussed) and the concentration of the hydrogen ions are diminished in the same proportion, and we can arrive at the exponent of the hydrogen ions in the real dough by adding the $\log. 6.5 : 44. = 0.83$ to the "diluted" dough. In fact the experiments which I have made in comparing the hydrogen ion concentration of diverse "diluted" doughs, in the proportion of 6.5:44 and 6.5:17.6 (the latter being the greater dilution and capable of being measured electrometrically without difficulty) has given as a result that the pH of this last dough was, at most, 0.1 lower than the first, then calculating according to the dilution, the concentration of the hydrogen ions should be 2.5 times greater, or the pH of 0.4 $\log. 2.5$, less than the last than in the first.

The fact is probably that flour contains substances which might act as "buffers" (1) (proteins, amino-acids, phosphates, etc.) and also conditions of dissociation and hydrolysis exists which escape direct measurement.

Also the configuration of the different curves relating to different flours, having different optima, we see that the concentration of the hydrogen ions is not the sole factor having influence on the baking value of a flour; if it were so, the curves would coincide. However, the divergencies met with in this regard should not be wholly placed to the account of the flour, for the experiments in the baking of flours No. 1-10 were made by one baker, while the other by still another one, a fact which introduces a personal element not altogether negligible. However, if this fact constitutes a disadvantage, in that it renders a comparison among the different experiments difficult, it is none the less true, that there is furnished more proof of the real existence of the optimum in question, by the circumstance that the optimum is not only verified for different flours and for different acids, but also by the experiments made by two different persons.

In that which concerns the effect produced by the different acids, there is nothing in our experiments to indicate that their optimum would be situated at different hydrogen ion concentration. The divergencies met with in this report are naturally to imputed to experimental errors.

Among my series of experiments, there are two which lead to the belief that the action of the acid may

also play a role; there are those made with phosphoric acid added to flour No. 11 freshly milled (Table II) and to the same flour set aside for a certain time (we shall speak later of this last series Table V and diagram IV.) In these two series, in fact, it appears that the Phosphoric acid has produced an effect, notably greater than that of hydrochloric or lactic acid.

Now it is known that in later years, phosphoric acid has been frequently recommended as apt to "ameliorate" flour. I have therefore, made this the object of a special research, with the view of establishing if it is really able to exert any influence other than that due to its hydrogen ions. It is this which has brought me to undertake with flour No. 12, a series of experiments, in which, with the aid of hydrochloric acid, I have prepared solutions which gave to the dough the concentration desired in hydrogen ions, and which was followed by a solution of an alkalin phosphate having the same hydrogen ion concentration as the "diluted" dough, in such a way that this concentration was always the same, whether the dough was prepared from a solution containing only hydrochloric acid or the solution employed contained phosphates at the same time. The result of these experiments are found in Table IV, which shows equally well how important it is to compare, among ourselves, experiments carried out simultaneously.

As is seen, this table is divided into vertical and horizontal sections. In the experiments figuring in the same horizontal series, the doughs contain the same proportion of phosphoric anions (noted in the vertical column) but with different concentrations with respect to their hydrogen ions. In the results tabulated in the same vertical column, the ionic concentration is the same and corresponds to

(1) That is to say, a concentration of hydrogen ions slightly below that of a solution M-15 of the primary phosphate, and almost equal to that which, according to the researches of S. P. L. Sorensen and E. Jurgensen, represents the optimum of the coagulation of protein material. See these same *Comptes Rendus*, 10, 1 (1911.)

1 See S. P. L. Sorensen, loc. cit.

the exponents of the hydrogen ion concentration marked at the head of each column, while the proportion of phosphate varies. For the quantity of phosphates, we have taken as unity the content in acid phosphate found in the natural state in the flour. Hence, in the series where the quantity of phosphate is 1.000, we have added none.

If the variations made are apparently quite small, it was because they should be sensibly of the same order of magnitude as those encountered in flours coming from different sorts of wheat, particularly with respect to that portion soluble in water. I have given the results of each particular baking as well as a number indicating the date of it, and I have calculated the mean of the groups of three bakings as ordinate.

A more profound examination of Table IV shows that the addition of phosphates has produced no effect in this case, or if any is to be seen, it is not favorable. As a matter of fact, notwithstanding the results, it is possible that in other cases phosphate ions may be able to exert a favorable influence, but although this may be so, their influence would never be of a nature as general as that of the hydrogen ions.

A comparison of the experiments made on different days, but always under the same conditions, will show likewise the need of comparing among themselves, as far as possible only the simultaneous experiments.

C. CONCLUSION

1. Upon the Storage of Flour.

One might object that the statements we have made are only of secondary interest; for if in the flours, or, to be more exact, in the dough made from them, there does not exist a hydrogen ion concentration other than such corresponding to an exponent of hydrogen ions from

pH = 6.5 to pH = 6.0 and it is between these narrow limits that are found the concentration in the flours examined, with one exception, which will be spoken of later, it is evident that we are not yet reaching a solution of the problem which alone is of technical interest; that is to say, that of knowing what determines the different baking values of different kinds of flour. We will admit that we have not yet exhausted the subject, and that we have perhaps barely touched the bottom of the question, yet we like to think that the results obtained are not without certain interest.

In fact, as we have indicated, all the samples of flour used were freshly milled, or nearly so. Now it is a known fact that flour improves with age. The reason for which a number of investigators have vainly sought the cause (1). We know, among other things, that flour turns sour in time (2), without knowing exactly the reason; that some believe the reason lies in the oxidation of one or the other of the substances in the flour while others—among them A. Kossawicz (3) who, however, has not furnished the proof to support his views—has invoked bacterial action. We do not know with certainty what the constituents are in a flour, which gives rise to acids. It appears that Aime Girard (4) had reason for stating that it is the fatty material which undergoes oxidation. Be that as it may, it is certain—and my own experiments have permitted me to

(1) See for example M. P. Neumann, *Zeitschr. für das ges. Getreidewesen* 1,289 (1909); 3.83 (1911).

(1) See for example, Report of the Home-Grown Wheat Committee for the fifty Season 1905-6 delivered at a meeting held in Guildhall Windsor, on July 12, 1906, page 6-7 Discussion.

(2) See, among others, Ballard, *Journ. de Pharm* (5) 8,387 (1883)

(3) *Einführung in die Mycologie der Nahrungsgewerbe*, Berlin 1911, p. 104.

(4) *Ann. de chim et de pharm.* (6) 3,289 (1884)

verify it—that a prolonged storage causes a diminution of these materials and that at the same time, the flour becomes very sour.

Finally, we know that a flour which has been milled for a long time develops an excessive sourness, and, in consequence, it is not good for bread making although, in this case, it is better to be mixed with a fresh flour which is too "weak", and which, thanks to the mixture, acquires the requisite "strength" (1). In the "diluted" doughs, made from small samples of flours which have been held for some time and under favorable conditions, I have observed an ionic concentration corresponding to a value of the pH equal to about 4, acidity somewhat stronger than that found of no importance, compared with the optima determined. In view of these facts, the results at which we have arrived, have suggested the idea that the essential effects in the storage of flour consists in an increase in acidity, which approaches the state where it would give to the dough the optimum ionic concentration, a state which the flour attains but even exceeds. However, this conclusion is not in the least premature. In fact, among the experiments, the results of which are given in Table II, is one which militates in its favor.

I have mentioned the first experiment of the series carried on with flour No. 12, to which acetic acid was added. This series of experiments was carried out when the flour was about one month old, and comparing this experiment with the first experiment of the hydrochloric acid series, which was effected when the flour was fresh, we see that the concentration of the hydrogen ions of the non-acidulated dough, has increased with the age of the flour, the value of the pH having decreased from 6.10 to 5.90, the specific volume having increased at the same time. But an

isolated experiment does not warrant one in drawing definite conclusions, inasmuch as the differences found between the two values is relatively insignificant.

However, in Table II, we may see three other series of experiments upon flours a little older, those carrying the numbers of 14 and 16. Their age is unknown to me; but they were at least older than one month, having come from England and were considerable time en route; we know nothing positive of their age other than the time of shipment. It is noticed that these are the flours which possess the greatest baking value, that is to say, the loaves made from them had the greatest specific volume and which is demonstrated by the "notes" given, for on all the other points they have been very nearly perfect. It is then to be presumed that storage has its effect; among other things, one of the two samples, No. 14, had merely been "ameliorated" by the addition of an old sour flour. We have here run across a flour by accident, which had a totally different color from the rest and which was strongly acid. Nevertheless, in the dough made without the addition of acid, the concentration of the hydrogen ions did not exceed $\text{pH} = 6.00$, and consequently the addition of acid would here still exercise undoubtedly a favorable action, although in the series made with phosphoric acid it was insignificant.

With the idea of learning how little is the influence of storage on flour, we have undertaken the experiment of baking with some of the samples already experimented on previously (No. 8, 9, 10 and 11) after having kept them for some time. These results are brought together in Table V and Diagram IV.

We may see from this table, especially in comparing the results obtained with the fresh flour, and which are found in Table II and III,

that we have not succeeded in elucidating this question. In fact, these experiments show that the samples had become a little too acid and that in one of them No. 8 it had become so in a very pronounced fashion. It is only in the case of No. 11 that there appears to be a question of "amelioration." In this sample it is even more notably marked than when submitted to a modification of its hydrogen ion concentration. Therefore, seeing that in this case the experiments on the old flour were made with the help of baker other than the one who baked the fresh flour, it follows that the experiment has little or no value. These experiments seem to show in some fashion that the effect of adding acid becomes weaker with time, although the optimum appears to be a little less marked. As to the prejudicial influence exercised, according to curve corresponding to No. 8, by a small amount of acid, it would surely be laid to experimental errors.

So as to be able to announce something positive on the subject of the effects of storage, it would be indispensable to bring about in many ways, more largely extended experiments. Circumstances have not made it possible, up to the present, but I hope later to be able to give more complete experiments, in view of which I have already done the preliminary work. If I have thought it my duty to incorporate in the present memoir these preliminary experiments, of which one may read the summary, it is for the sake of completeness as well as to obviate premature conclusions.

2. Artificial Means of Ameliorating Flour.

Although the results we have obtained do not respond in a complete fashion to the question relative to the phenomena taking place during the storage of wheat flour, they have, nevertheless, in my judgment, solved

in a large way, another problem of great interest to millers and bakers.

It is known that, in all other cases, where something is used to "ameliorate" a flour which for any reason does not respond to the requirements, recourse is had to different proceedings more or less suspicious, notably by adding alum, or even sulphate of copper, (1) and sometimes sulphate of zinc (2). However, as these additions have at all times and justly so, been regarded as adulterations, it is quite natural that there were no persons who appeared to have, so to speak, any exact knowledge of the cases in which they were used. I have myself been unable to put my hand on any work of Kuhlmann, d'Accum or of Mitchell, who, after Peligot (3) and V. Bibra (4) in which they specially occupied themselves with this question.

V. Bibra (5) expressed himself thus: "When flour is moist, often from various other causes, the protein decomposes more or less, and loses the property of binding, becoming soluble in water. The addition to such spoiled flour of the mentioned substances gives to the protein the capacity of making dough again, inasmuch as the alum or the sulphate of copper forms a compound with the protein in which it becomes again insoluble in water." Peligot (6) on the contrary simply says that he is unable to explain why the sulphate of copper acts favorably upon the appearance of the bread, but it is certain, he adds, that it is of service. The employment of this substance had become general in Belgium in 1816 and 1817; from there it spread to France and no person would guar-

(1) See Bibra, *Die Getreidearten und das Brod*, Nurnberg 1860, page 388, and Peligot, *Traite' De Chimie analytique applique'e a l'Agriculture*, 1883, page 394.

(2). Peligot, loc. cit. (3) loc. cit. (4) loc. cit. (5) loc cit. (6) loc. cit.

antee that it had completely disappeared."

In that which concerns the explanation given by V. Bibra of the effect produced by alum, it appears that he did not have the support of any experiment. Although he may have made one, it was not conclusive, as I have assured myself by trying to extract the gluten from a sample of old flour mentioned above and which has been stored so long that it had become strongly acid (pH of the "diluted" flour—about 4). To this end I have prepared two pastes, the one with water, the other with a $\frac{1}{2}\%$ alum solution, but notwithstanding all my care, I have obtained gluten neither from the one nor the other. It also appears that there is little probability of a flour, already strongly acid, being "ameliorated" by adding a substance which, as in the case of alum, is itself still more acid (a colorimetric determination made upon the $\frac{1}{2}\%$ alum solution permits me to state that its pH = 3.81). According to V. Bibra (1) Liebig, on the contrary, would have "ameliorated" the flour which had become too old, by making the dough with lime water. This accords perfectly with what we have been able to establish on the influence of acidity.

If, on the contrary, we admit that there are freshly milled flours or flours which have not been ameliorated sufficiently fast by storage—and the flours are very different among themselves as relates to the speed with which they mature (2)—which has been the object of these manipulations, the explanation in so far as it concerns alum, is very simple. It is that alum is a salt with a strongly acid reaction, which added in the proportions indicated, has the effect of increasing the concentration

of the hydrogen ions, and consequently, ameliorating the bread.

As regards the sulphate of copper, this explanation does not suffice. It is true that it is a salt having an acid reaction; but the amounts which have been employed have been so small— $\frac{1}{4}$ part per thousand at most—that its influence on the ionic concentration in the dough would be nil, and an experiment which I have made with this product has demonstrated to me that it is only on a flour of a special sort that it is capable of producing a favorable effect. However, the extended use it has had, according to Peligot raises the suspicion that it has not been added to flour which had become spoiled after milling. It is more likely, I think, that the flour thus treated came from spoiled wheat, such as is met with in bad years. Unfortunately, it has not been possible for me, up to the present time, to procure samples, and that is why I am unable to say how such flour would act.

That the explanation given above is essentially correct so far as it concerns alum, is for the reason that I have demonstrated it by a series of experiments on flour No. 11 and which had been stored for some time, a series which was made simultaneously to that given in Table V and represented in diagram IV and with the same flour.

I made three experiments in which I prepared dough one degree with pure water, 2 degrees with a $\frac{1}{4}\%$ alum solution and 3 degrees with a $\frac{1}{2}\%$ alum solution, which are the amounts apparently which according to V. Bibra, have been employed in practise. Following are the results obtained:

Experiment	1	2	3
pH	6.00	5.55	5.35
Specific Volume	3.46	3.81	3.68

That is to say, just the effect expected, in view of the other properties of the bread found to be amelio-

(1) loc. cit. (2) See for example M. P. Neumann Jour. for das ges Getreidewesen 1,289. (1909).

rated in the same fashion by the addition of acid.

However, this would be of less interest if these domestic remedies, more or less under suspicion in the older days, were being used more openly in our day, under one form or another. In fact, in recent time—and especially in England it seems—attempts are made, and often even under patents, with different processes, having for their object the “ameliorizing” of flour, or of artificially “aging” it, by means of some addition; that is to say, to give it, at the outset, those qualities which it acquires only after a more or less prolonged period of time. With one exception, of which we shall speak later, all these methods consist essentially in adding to the flour one or the other of the acid salts, or some acid. Some one has even patented a process consisting in causing a current of air to act on flour which air has previously passed through a receiver filled with phosphorous pentachloride. Often the acid phosphates of calcium are employed, alleging as a reason or excuse that by such means the nutritive quality of the flour is augmented, a quality which they say has been diminished because of the fact that the envelop (bran) which carries the largest amount of ash and consequently the phosphates of the flour, has been removed in our day from the superior flours.

It is evident that this method of procedure is explained by what we have shown above, and that there is perhaps reason to believe that they will give it up, even if the legislature of the different countries do not feel like taking up the question of intradicting all these kinds of manipulations, of which there has been a great question recently in England. In fact, all bakers actually dispose to a wholly simple and most honest means of remedying whatever is lacking in

flour in this respect, it is only necessary to add to milk or any other liquid in making the dough, a convenient concentration of hydrogen ions, which may be done in a perfectly unobjectionable fashion.

The experiments given below show that even if the dough is made with milk, the optimum concentration of hydrogen is greater than that of a dough made from fresh milk and of flour without any addition. In these experiments I have made use of skim milk and of flour No. 11 and I have added varying amounts of lactic acid, with the following result:

Milligram equivalents of lactic acid added to 1 kilogram of flour					
	0	6.9	13.8	20.7	27.6
pH	6.45	6.25	6.05	5.80	5.60
Specific volume	3.34	3.44	3.40	3.64	3.62
Note	7.77	7.81	7.53	7.73	7.81

As may be seen, the addition of acid here likewise increased sensibly the specific volume. If the “note” given remains essentially constant, this holds likewise for the bread made without the addition of acid and which was nearly perfect.

In the two experiments where I added the greatest quantity of acid, the milk was coagulated on heating, without noticing it, however, when the bread was once baked.

3. Concentration of Hydrogen Ions of Diverse Products of Grinding.

Besides the means of “ameliorating” the flour mentioned in the preceding, it remains for us to mention one of a totally different nature, to know the aqueous extract of bran recommended by M. A. E. Humphrey in sundry reviews of English Milling (1) as being susceptible in certain cases which are not specified, of exercising a most favorable influence on the baking value of a flour.

At first sight, affirmation seems to accord very strongly with what we

(1) See for example, supplement to the Journ. of the Board of Agriculture, Vol. XVII, No. 3, June 1910, page 43. Also Milling Feb. 4, 1911, page 108, and Oct. 23, 1909, page 478.

have said on the importance of ionic concentration, accepting the belief of all the older savants who occupied themselves with this question, this being the exterior portion of the grain of wheat possessed the highest acidity. Baland (2) for example, expressed himself as follows with figures to support it: "The farinaceous parts of the grain which pertain to the outer envelope is more acid than the central portion."

On the contrary, this hypothesis is not in accord with the one announced by De Parmentier, who after Balland (1), knew that the addition "had for effect the rejuvenation of old flour," in other terms, restoring flour which had become too acid.

However, *this supposition that the exterior portion of the grain of wheat is more acid than the central portion, is not exact; it is wholly contrary to the truth; it is the central portion which is the most acid, which has the greatest concentration of hydrogen ions.* We can easily explain the reason for this error; it depends on the manner in which one has determined the acidity, and we have here a conclusive proof of the thesis of S. P. L. Sorensen given above and according to which one is unable, following the example of the older investigators, to determine by titration the concentration of the hydrogen ions, that is to say, the real degree of acidity.

If, in fact, we prepare the aqueous extracts of different products of mill-

ing the same wheat—for example 36 per cent of the first flour, 36 per cent of the second flour, and the rest bran—when we add phenolphthalein to each of the three extracts in order to titrate them, with sodium hydroxide to a red color, we arrive at the same result, it is true, as Balland; that is to say, we determine that the flour of 0-36 per cent demands in order to produce the red color the smallest quantity of alkali, while the flour of 36-72 per cent requires a little more and the residue much more, result which follows the idea formerly held, that is to say, that the residue constitutes the produce which is the most acid.

But when, in the same extracts, we come to determine the concentration of the hydrogen ions by electrometric or colorimetric methods (1a) we find that the extract of bran has the lowest hydrogen ion concentration which is increased in the ordinary flour and attains its maximum in the finest, coming from the central portion of the grain.

As an example, I shall cite an experiment below. Nevertheless, I might cite a great many; in all cases I have never found an exception.

I prepared an aqueous extract by the process which was always used in this work, by treating, for two hours, one part of the flour or bran (the latter ground as finely as possible in a coffee mill) with four parts of ice water and filtering the mixture.

Submitted 50cc of the liquid to titration, to a red color, in presence of phenolphthalein. Used -----
In measuring these same liquids electrometrically we find the pH -----

Flour 0-36%	Flour 36-72%	Bran
0.55cc	0.78cc	3.5cc N/5 NaOH
6.06	6.14	6.55

(2) C. r. 97, page 348, and Journ. de pharm. 5, 8 page 347 (1883).

(1) C. r. 97, page 651 (1883). I have been unable to procure the original memoir of de Parmentier, work which is probably dated the last quarter of the 18th century, an epoch during which de Parmentier interested himself greatly in all which concerned the panification of wheat.

We see, therefore, that the finest flour, that which comes from the interior of the grain, is in reality the

(1a) The colorimetric measure of an aqueous extract of bran is quite difficult because of its own color.

most acid, in that it possesses the highest concentration of hydrogen ions, and that on the contrary, it contains, compared with the exterior of the flour, a smaller proportion of phosphates or of other substances capable of acting as a "buffer" (2). Consequently, notwithstanding a greater concentration of hydrogen ions, the fine flour requires a smaller quantity of sodium hydroxide than that required by the residue to lower the concentration in question to a value at which is situated the point where phenolphthalein turns in color.

From the preceding, we understand why Parmentier found that the addition of bran is proper to "rejuvenate" old flour; but we understand less why Humphries was able to obtain favorable results by adding bran to a freshly milled flour. Also, in some bread made by adding the extract of bran, a series of experiments has permitted me to verify a decreasing specific volume at the same time as that of the decrease of the hydrogen ion concentration, regularly although in small degree, in proportion as the amount of extract of bran was increased.

On the other hand, the fact should be recalled here that the extract of bran constitutes a most favorable medium for bacteria and, in consequence, if we are able to admit that, in preparing some of the extracts used in his experiments Humphries neglected to take sufficient precautions to prevent the action of the organisms, so that the extracts in question became acid, then the results obtained by the English savant is easily explained from every point of view.

4. Extraction of Gluten Used as an Analytical Method.

There only remains for us to speak of a certain fact having some relation to these researches.

If, with the intention of obtaining the gluten by washing, we make a

paste with a certain flour, using an acid mixture which according to what has preceded has furnished the best results in the experiments on baking, it will be noticed that the paste immediately takes on a consistency a little more viscous than that which has been made with pure water; but when it has stood about an hour, it makes an excellent impression, being thickened and elastic, precisely as it should be. However, if we attempt to obtain a portion of the gluten by washing, we will obtain none; the whole melts and falls to a powder, even if washed with the greatest precaution in passing it over the finest silk sieve; and even an amount of acid considerably weaker than that giving the optimum specific volume and of baking value in general, completely hinders the formation of gluten.

It was thus that I attempted to extract the gluten from flour No. 11 (Table II) by making a paste with the liquids used in the first four experiments with hydrochloric acid. Here are the results:

1-25 grams of flour and 15cc of distilled water. Exponent of the hydrogen ions of the "diluted" dough $\text{pH} = 6.10$. 8.3 grams of crude gluten was obtained, a little "short" perhaps, but otherwise of good quality.

2-25 grams of flour and 15cc of the acid mixture. ($\text{N}/42 \text{ HCl}$). pH of the "diluted" dough = 5.05.

It was impossible to obtain even a coherent gluten. The whole melts into particles which pass through the sieve and obstruct it in part. However, at the outset, the paste had a very fine appearance; it appeared to be more successful and of a satisfactory tenacity.

3 and 4—with the acid $1\frac{1}{2}$ -2 times stronger than in 2, identical results were obtained and it was the same in an experiment made with phosphoric acid of a concentration of the hydro-

(2) S. P. L. Sorensen, loc. cit.

gen ions was similar to that of the "diluted" dough.

It appears then, that already in experiment 2, the amount of acid is sufficient to hinder the formation of gluten, even though it is only the double proportion which gives the optimum of baking value.

Now it is a fact known for a long time, that the yield of gluten is diminished by the addition of acid to the

A	1.	25 grams of flour plus	0cc	-	-	-	N/5 NaOH = 15cc water
	2.	25 grams of flour plus	2.7cc	-	-	-	N/5 NaOH plus 12.3cc
	3.	25 grams of flour plus	5.3cc	-	-	-	N/5 NaOH plus 9.7cc
	4.	25 grams of flour plus	8.0cc	-	-	-	N/5 NaOH plus 7.0cc
B	1.	25 grams of flour plus	0cc	-	-	-	N/5 NaOH plus 15 cc water
	2.	25 grams of flour plus	2.8cc	-	-	-	N/5 NaOH plus 12.2cc water
	3.	25 grams of flour plus	5.6cc	-	-	-	N/5 NaOH plus 9.4cc water
	4.	25 grams of flour plus	8.5cc	-	-	-	N/5 NaOH plus 6.5cc water

dough, in all cases, if the amount passes a very narrow limit (1); and it is a fact also that old acid flours do not furnish gluten. But it has been recognized that the diminution or the disappearance of the gluten is due to the increase in acidity. On the contrary, just as Balland says (2) "The acidity in old flours is not, as has been admitted, the cause of the disappearance of the gluten; it is of no consequence; it does not precede the alteration, it follows it." However, in the place cited, he furnishes no proof to support this assertion and I have likewise not found it elsewhere. It is strange that neither he nor other investigators have the idea of trying if, in neutralizing the acid, an acid flour would not recover its power of furnishing gluten. I have been able to verify in fact, that this is so; the experiment below being

carried on with an old acid flour mentioned previously, to demonstrate it.

To give to the "diluted" dough a slightly acid reaction to very sensitive litmus paper (pH — 6.5 nearly) one of the flours A, required the addition of 8cc of N/5 sodium carbonate to 25 grams of the flour; the other B 6.5 cc.

With each of the flours, four pastes were prepared:

In washing these pastes in the usual fashion on a silk sieve, we obtained:

A-1. Not the least trace of gluten.

2. Likewise none; however, it was noticed that the wet mass had a certain tendency to "roll up" on the sieve to form small "sausages" which, however, melted little by little.

3. 4.5 grams of crude gluten, very "short" and non-elastic.

4. 9.8 grams of gluten, also 'short' and not the easiest to collect.

B-1. Not the least trace of gluten.

2. Likewise none, the mass on the sieve showed a very slight tendency to "roll up."

3. 2.4 grams of crude gluten, very "short" and friable absolutely devoid of elasticity and difficult to collect.

4. 8.4 grams of crude gluten of passably good quality although somewhat "short."

These experiments in which we have added acids to freshly milled

(1) See W. Johannsen, Om Gluten og dets Plads i Hvedekornet, Meddelelser fra Carlsberg Laboratoriet 2,332 (1888). Resume in French, 199.

(2) C. r. 97. 751 (1883).

flour, as well as to old flour, seems to demonstrate that

1. *The diminution in the gluten content, which, it is said often takes place when a flour, on aging, becomes more or less sour, is due only to the dissolving action on the gluten exercised by the acid formed, and not (at least not in an appreciable fashion) to a transformation of the components of the gluten.*

In reporting on what has been given above on the subject of the importance of concentration of the hydrogen ions for the baking value, we see, also that

2. *The extraction of gluten by washing should be definitely and irrevocably considered as being without value in so far as the analytical method serves to determine the industrial value of a wheat flour.*

As a matter of fact, experience has shown in the long run, that the extraction of gluten is of no value in this respect; but nevertheless, up to recent times, people have been much occupied with this question. In my judgment it will serve nothing to continue this work.

I do not pretend to prejudge the question relative to the role played by the gluten content of flour, that is to say, in protein or nitrogenous substances insoluble in water. My appreciation relates only to the manner of proceeding to determine this content.

RESUME:

1. For the dough of any wheat flour, there exists a determined concentration of hydrogen ions, with which the production of bread from this flour will be the most successful, and this concentration is greater than that which is found in a dough made from the flour in question freshly milled and prepared with pure distilled water or fresh milk.

2. This optimum concentration corresponds approximately to the exponent of the hydrogen ions $\text{pH} = 5$;

for choice flours this appears to be a little higher; for the ordinary or bad kinds, on the contrary, it is slightly lower.

3. Of the different products obtained from the milling of the same wheat it is from the finest flour—that which comes from the central portion of the grain—which has the greatest acidity, that is to say, the greatest concentration of hydrogen ions, while the bran is the least acid, the lowest concentration of hydrogen ions.

4. The different artificial means preached in recent times as being capable of ameliorating flour, none are of value other than that of increasing the hydrogen ion concentration in the dough.

5. The opinion expressed by several savants of other days (according to whom, the addition of alum was formerly utilized) that it was supplied to spoiled flour, that is to say, to flour which had spoiled after milling is certainly not correct.

6. The extraction of gluten by washing in so far as the analytical method serves to determine the baking value of a flour, is without any value.

May I be permitted to observe in closing that these experiments which I have just described constitute, fundamentally, only one part of a more extended piece of work, of which the goal is to determine the correlation existing between the chemical composition of flour and its baking value. However, as this work is still far from finished, and as, nevertheless, the experiments above described appear to me to result in conclusions of some interest, I have believed that there should be no longer a delay in their publication, altho I know better than anyone that, up to this point, these experiments present a purely provisional character. Also, if I have the time and strength, I have the intention to follow up this work and to

complete it in the necessary direction.

In conclusion, I must pay to my Chief, Professor and Doctor, S. O. L. Sorensen, the homage of my great gratitude for having been willing to grant me the leisure to do this work, as well as having aided me with his counsel. I have to thank equally, M. R. Rubow, director of the baking company Malmo stora Valskarvn et Malmo, who gave the first impetus to these researches and who has constantly given me valuable backing.

I owe, likewise, my sincere thanks to my colleagues M. M. S. Palitzsch

and E. Jurgensen, who took charge of the electrical measurements; also to M. C. A. Streenstrup who has aided me in many ways.

Finally, there remains to mention, with a strong sentiment of recognition, that the number of experimental bakings were made by M. A. Horup "contre-maitre" of the company mentioned above and M. J. Rasmussen, master baker at Copenhagen, without whose intelligent and indefatigable zeal, I would have accomplished nothing.

July, 1911.

Relation of the Crude Fiber Content of the Wheat to the Feed Obtained

L. H. McLaren

The relation between the percentage of crude fiber in the wheat and in the feed seems to have been given little consideration. We determine the percentage of crude fiber in the feeds at the beginning of each crop year and then set our standard for that year. Little attention has been paid to the actual fiber content of the wheat and its effect upon the composition of the feeds.

It has been the claim that certain types of wheat would give a feed with a higher percentage of crude fiber than other types. Since the question of feed control has become of such prime importance it was decided to give this matter some attention. There are several factors to be taken into consideration in a question of this kind, as the quantity of bran and other feeds obtained from the wheat and the amount of crude fiber present in the products obtained. For example: Does a wheat which gives a large percentage of feed necessarily have a high percentage of crude fiber in the feed obtained? It seems reasonable to suppose that this would depend more upon the type of wheat,

but at the same time a certain relation may exist.

Our plan was to mill the various types of wheat in as nearly the same manner as possible. As the percentage of crude fiber in the feed can be changed to a certain extent by the manner in which the wheat is milled, we have tried to eliminate this factor by careful operation of the mill. Therefore our results may not compare to a large mill but they will at least be comparative.

The question has been asked if a wheat grown in a cold climate would not have a heavier bran and a more fibrous feed than a wheat grown in a warmer climate. Enough work has not been done to answer the question positively but our results would indicate that it depends more upon the character of the wheat than the climate in which it is grown, although that grown in a cold climate seems to have a little heavier bran. The weight per bushel of the wheat probably affects the character of the feeds more than any other factor. It may be possible that the yield of flour could be determined by some relation

between the crude fiber of the wheat and the weight per bushel.

Type samples of wheat were obtained of the various kinds of wheats from last year's crop (1920). These samples were milled on an experimental mill and since the separation of the feeds into various grades is more or less arbitrary no attempt was made to make any separation in the feed other than bran and the remaining feed is designated as midds. The feeds obtained from our mill are not as free from the low grade flour as those obtained from a large mill but we believe that our results are comparative. The bran obtained also has probably more flour adhering to it than that obtained from a large mill but not enough to seriously affect the percentage of crude fiber. The results show the percentage of crude fiber in the bran and midds. The percentage of crude fiber in the total feed is calculated from the percentage of bran and midds obtained in terms of each other.

The results obtained indicate as mentioned that the wheat grown in cold climate does have a little heavier bran and makes a more fibrous feed than one grown in a warmer climate. For example: X50 is a Dark Hard Montana wheat while X51 is a Dark Hard Kansas wheat, the Montana gives a feed with a total crude fiber of 7.25% while the Kansas wheat gives a feed of 6.96% crude fiber. The increase here is slight but of course these are individual samples and what the average of a number of samples would be is hard to say. Another comparison may be made between the light weight wheats and the heavy weight wheats of the same character. It will be noticed that the light weight wheats give a much more fibrous feed than the heavy weight wheats. This is what might be expected and the greatest difference is between these two types. The weight per bushel is probably the greatest factor affecting the percentage of crude fiber in the feeds. The light

		Grade	Wt. per Bu.	Crude Fiber Wheat	Percent of Bran	Percent Crude Fiber Bran	Percent of Midds	Percent of Crude Fiber	Percent Crude Fiber Feeds
X40	1	DNS	62	3.32	49.75	10.63	50.25	2.79	6.70
X41	1	DNS	59½	3.40	51.75	11.39	48.25	2.95	7.32
X42	1	NS	62	3.19	49.00	10.30	51.00	2.64	6.40
X43	1	DNS	60	3.25	55.00	9.75	45.00	2.88	6.60
X44	1	NS	59	3.57	58.00	10.42	42.00	3.25	7.40
X45	2	DNS	57½	3.41	59.00	10.19	41.00	2.81	7.15
X46	2	DNS	57	3.81	59.75	10.15	40.25	3.64	7.53
X47	3	DNS	55½	4.25	62.50	10.67	37.50	4.14	8.22
X48	3	DNS	55	4.27	62.80	10.80	37.20	4.31	8.38
X49	4	DNS	53	4.40	64.20	11.70	35.80	4.07	8.97
X50	1	DHW	60½	3.30	50.36	11.30	49.64	3.15	7.25
X51	2	DHW	57½	2.96	58.79	10.03	41.21	2.59	6.96
X52	1	HW	60	3.17	57.18	8.84	42.82	3.08	6.78
X40	Canadian Marquis					X47	Minnesota Spring		
X41	Montana Marquis					X48	Minnesota Spring		
X42	Soft Canadian Spring Wheat					X49	Minnesota Spring		
X43	Hard Montana Spring					X50	Montana Hard Winter		
X44	Soft Montana Spring					X51	Kansas Hard Winter		
X45	North Dakota Spring					X52	Kansas Soft Winter		
X46	Minnesota Spring								

weight wheat not only gives a large percentage of feed, but the product obtained also has a higher percentage of crude fiber.

Another point of comparison may be made between the hard types of spring wheat of the same weight and the softer types. It will be noticed for example, X40 is a hard Canadian wheat which gives a feed of a crude fiber of 6.7% while X42 is a soft Canadian wheat with a feed of a crude fiber of 6.4%. However, there is a little difference between X41 and X44 which is a hard and soft type of wheat.

To determine the yield of flour from the wheat based on its crude fiber content is very possible. However, various factors enter into it and makes the yield as determined from the crude fiber somewhat different than that obtained from the mill. The theoretical formula for such a determination would be:

$$\frac{\text{Crude Fiber Feed} - \text{Crude Fiber Wheat}}{\text{Crude Fiber Feed} - \text{Crude Fiber Flour}} = \% \text{ Flour}$$

Our results along this line are not complete enough to publish and would be somewhat misleading.

Importance of the Value of the "Absortive Capacity" of the True Gluten and of Its Practical Use in Flour Analysis

Henry d'Andre

The fixing of the baking value of flours cannot be done by only taking into consideration the quantities obtained in flour analysis for ash and dry gluten, as though the ash had an exact relation to the grade, and the dry gluten, a relation with the strength of the flour and with the proportional contents in protein, these determinations are not sufficient to give even an approximate value as to the quantity of water the flour will absorb in kneading and consequently its yield in dough and bread.

For these reasons, it has been necessary to establish by a preliminary reduced trial of baking, the baking value of flours which are then expressed by the following statement: Loaf volume, loaves per barrel, weight of bread, used water, fermenting period, stability, etc., but such determinations although excellent cannot serve as a base to the conditions of practical baking, as the factors obtained in such reduced testing of baking only have comparative values for flours treated in the same

way. The proof of it exists in the fact that the principal analytical American laboratories recommend baking tests on reduced scale and in accordance with a formula, simply to determine comparatively the volume and colour of bread, and to accentuate the qualities and defects of the flours, but not to produce bread having the same qualities and appearance of the commercially prepared bread.

This restriction makes the reduced baking test lose all its practical value and loads unnecessary flour analysis with a determination which results cannot be considered at their exact value, as is the case of the datas obtained for ash, moisture and dry gluten in the flour.

Nevertheless there exists an extremely simple and rapid method for determination of the faculty of absorption of water by the wet gluten of which depends essentially the quantity of water absorbed in kneading. This value which gives also an accurate measure of the qualities of the true gluten allows to judge imme-

diately the real grade of the flour and therefore its baking value and the result that same can give in the baking test.

This factor which takes the name of "absorptive capacity" on the wet gluten represents "the quantity of water the wet gluten is susceptible of retaining after being squeezed," and expresses the quantity of water contained in one hundred parts of wet gluten squeezed.

This quantity is calculated by the following formula:

$$\text{Absorptive capacity} = \frac{(W-D) \times 100}{D}$$

W, being the weight of the wet gluten,
D, being the weight of the dry gluten.

The exact determination of the absorptive capacity of gluten and consequently the practical value of this data requires utilizing an accurate method for the extraction of the wet gluten and for its squeezing, obtained in practice by a double-roller drying machine, which allows results to be independent of the skillfulness of the operator. The wet gluten accurately weighed will be dried under 115° Centigrade for at least 14 to 15 hours, taking the precaution to cut it transversely so as to help its complete drying.

In the American methods of analysis, insufficient importance has been given to the exact determination of wet gluten owing to the fact that the percentage of moisture in the gluten has been considered as subjected to considerable variations.

Still, when once these variations have been systematized by making use of a convenient method, the calculation of these variations becomes the best and most accurate factor which can be used for verifying the qualities of the true gluten.

In a great deal of analytical reports expended by American laboratories, the obtaining of the percentage

of the wet gluten is mentioned as being procured by the percentage of the dry gluten multiplied by 3. This declaration is not correct, as it would lead one to suppose that every flour has indiscriminately a uniform and constant quality, whereas we are aware of the fact that absorptive capacity is essentially dependent on the grade, age and degree of granulation of the flour, and moreover of the class and originating point of the wheat milled.

If the ratio of gliadin and glutenin cannot be obtained rapidly in the analytical practice, the gluten quality must be determined at the same time as the percentage of dry gluten, because, for the baking value of the flour, the gluten quality is more important than the whole quantity of the dry gluten.

As the contents of glutenin increases in the true gluten, in the same way as the rate of extraction of flour, there will be, for each grade of milled flour, a higher degree of quality which must be appreciated by the absorptive capacity of gluten, in harmony with the contents of gliadin of the same gluten. See Table.

By the current use of the hydrating capacity of gluten, which is the base of all flour analysis, one will rapidly judge that the reduced baking test, so much in use in America, is not absolutely indispensable to be able to appreciate the baking value of flours.

If two grades of flour, of equal strength and class, are considered, the absorptive capacity of gluten alone will give, by its rapid determination, the exact measure of the comparative baking value of the two given grades of flour: the flour which will be supposed to give the best baking results will thus be really and clearly shown for the higher hydrating capacity obtained.

The following table shows the variations that the absorptive capacity of gluten undergoes, comparatively with the strength of flour, with the ratio

of milling extraction determined by ash, and with the contents of gliadin referred to 25 parts of glutenin:

Mill Streams	Percentage of Gliadin						Baking Value
	Wet gluten	Dry gluten	Absorpt Capacity	in the Flour	In the gluten of flour	To 25 parts of glutenin	
A	26.67	9.21	65.5	6.86	74.42	72.9	0.392
B 1	30.27	9.78	67.6	7.33	74.93	74.7	0.380
C	33.09	10.37	68.6	7.89	76.06	79.4	0.308
D	33.39	11.13	66.6	8.27	74.33	72.4	0.452
E 1	38.49	12.84	66.6	8.70	67.75	52.5	0.444
E 2	37.05	11.99	67.6	8.02	66.93	50.6	0.548
B 2	28.65	9.51	66.8	7.20	75.70	77.8	0.512
F	39.96	13.19	66.9	8.24	62.42	41.5	0.576
G	34.p6	11.52	66.3	7.68	66.63	49.9	0.512
H 1	36.21	13.47	62.8	7.77	57.66	34.06	0.844
H 2	36.09	13.28	63.2	7.95	59.90	37.3	0.680
J	33.30	12.80	61.5	7.27	56.81	32.9	1.200
K	33.55	14.05	60.5	8.05	57.33	33.6	1.680
L	37.41	14.20	62.04	7.98	56.22	32.1	1.548
M 1	34.11	13.34	60.8	7.52	56.40	32.4	1.600
M e	36.72	14.19	61.3	7.64	53.82	29.1	1.628
Offals	12.78	5.06	60.4	3.12	61.56	40.05	2.700
1st Break	23.58	8.52	63.8	5.43	63.67	43.8	0.532
2nd Break	21.75	7.74	64.4	5.49	70.96	61.1	0.432
3rd Break	33.00	11.60	64.8	8.36	72.08	64.5	0.612
4th Break	37.86	14.80	60.9	8.93	60.34	38.04	1.492
5th Break	31.38	13.06	58.3	7.90	60.51	38.3	3.112
II RM C1	34.56	12.29	64.4	8.22	66.91	50.5	0.608
II RM C2	36.96	13.17	64.3	8.78	66.67	50.01	0.592
2d Semita	32.37	11.50	64.4	7.59	66.19	53.6	0.436
X	25.11	9.59	61.8	6.54	68.19	53.6	0.824

Buenos-Ayers, July 10th, 1921

THE HUMPHRIES PROCESS. K. Mohs. *Z. ges Getreidewesen* 12, 89-103 (1921).—An attempt to explain for those unfamiliar with colloid chemis-

try the Humphries-Thomas process for treating and improving the baking qualities of wheat flour. Though

(Continued on Page 43)

WATER SOFTENING FOR BOILER FEED

M. E. Schulz

Weber Flour Mills Corporation

(Delivered before the Annual Convention of the Society 6-2-1921)

Many may think this subject has no place at a Cereal Chemists' Convention but many flour mills make their own power and the chemist that does not use his laboratory to analyze coal, oil, water for boiler feed, and flue gases is not giving his firm his full value.

The development of the steam boiler from the time of Watt to the present water tube steam generators of high efficiency took generations, and even today there are many plant

boilers working under low pressure with enormous waste of fuel and low efficiency of heating surface. The rate of evaporation in the older type of boilers with large water space and slow concentration caused little trouble from the use of bad water. Boiler designs become more intricate as the development continues and the rate of evaporation as well as the pressure is increased, therefore the feed water problem becomes one that warrants serious consideration, but

with the boiler feed problem as with everything else the crudest as well as the latest methods are in vogue.

Feed waters in use at present are, in most instances worse in quality than those in use in the early days of steam boiler operation. This is due to the increased industrial activity causing a pollution of the water supplies by introducing waste of all sorts into rivers, lakes, and their tributaries. These wastes consist of drainage from coal mines, waste from galvanizing plants, dye houses, paper mills, etc., as well as sewage from cities and towns.

The evaporation of water and of water only, as expressed by the chemist's formula H_2O occurs in the generation of steam. Few of the natural water supplies are pure, since carbonic acid absorbed by water when falling as rain, enables it to dissolve certain salts of lime and magnesia. Other substances will be dissolved, depending on the nature of the rocks, soil, vegetation, sewage, and industrial waste with which it may come into contact. Among substances in solution in waters are the following:

Calcium carbonate (carbonate of lime) which is but slightly in chemically pure water but when carbonic acid is present it dissolves in the water and forms the bicarbonate of lime which is soluble. Carbonate of lime alone will not form a hard scale, but when present with other substances which cement it, it is apt to form a hard scale.

Calcium sulphate is also quite common in all natural water supplies and is responsible for the hardest boiler scale. Further, this salt also acts as a cement, causing a hard scale formation with salts which ordinarily would form only sludge or a soft scale.

Calcium chloride is sometimes found in natural waters but it is very soluble and in absence of other scale forming salts will not form scale un-

less after great concentration. It, however, can be classed among the corrosive substances found in water, as after concentration in the boiler it may be dissociated liberating hydrochloric acid.

Calcium nitrate has practically the same characteristics as calcium chloride but waters containing it are comparatively rare.

Magnesium carbonate is more soluble than calcium carbonate, but is ordinarily found in water as a bicarbonate. Bicarbonate of magnesia has all the characteristics of calcium bicarbonate.

Magnesium sulphate is common in natural waters in which it is extremely soluble. Alone it will not form scale but is broken up by lime salts from which scale is formed.

Magnesium chloride is very objectionable, since it not only forms scale but causes corrosion by liberating hydrochloric acid.

Magnesium nitrate has the same characteristics as magnesium chloride but is usually present only in very small quantities.

The sulphates of iron and alumina are present in water supplies contaminated with mine drainage or the waste from galvanizing plants. These substances when present, act in the boiler exactly like free sulphuric acid inasmuch as they are dissociated by heat, the acid being set free and the iron and alumina precipitated as sludge or scale.

The oxides of iron and alumina are usually present in small quantities and have little bearing on the formation of scale.

Silica is also present in small quantities in nearly all waters. It is a scale forming substance but since it is rarely present in large quantities it is usually ignored.

Free sulphuric acid like the iron and alumina sulphates is introduced by drainage from mines and galvanizing plants. In the boiler it imme-

diately attracts the boiler forming sulphate of iron, which the heat decomposes, forming the hydrate of iron and free sulphuric acid. This acid liberated repeats its action upon the metal and thru an indefinite number of destructive cycles. The acid is non-volatile, therefore the amount of acid in the water in the boiler is constantly increased by the quantity introduced with the feed so that the decomposition of the boiler metal is in direct ratio with the concentration which occurs in the boilers.

Carbonic acid is present in its free state in all natural waters. Its presence in the boiler promotes pitting and corrosion. It is also the acid which holds in solution the carbonates of lime and magnesium.

Sodium sulphate, sodium carbonate, sodium chloride and sodium nitrate are neutral, non-scaling and non-corrosive salts and are not objectionable unless present in excessive quantities.

Steam generation is a continuous process; fresh feed water being supplied to the boiler as the water converted into steam leaves; since none but volatile impurities pass out with the steam, this results in a continued concentration in the boiler of the impurities introduced with the feed water. The non-volatile impurities collecting in the boiler manifest themselves as suspended water scale, corrosion, or by an increased density of the boiler water.

Suspended matter may be carried in with the feed or may be due to the accumulation of those substances that are forced out of solution as a result of either heat or concentration or by the combined action of both. Scale formation in the boiler is due to the action of heat, pressure, and the concentration on the impurities in solution and suspension in the feed water.

Corrosion of the boiler is due to the introduction of gases and acids

or their formation from some of the impurities in solution in the feed water by the reactions resulting from heat, pressure and concentration.

The increased density of the boiler water is due to the concentration of the sodium salts and of the scale forming salts to the limit of their solubilities.

That scale in the steam boiler is one of the great hindrances to the economical and safe operation is beyond question. It is feared by all steam users and their fear of expense and danger from it is shown by the large number of manufacturers of boiler compounds, purifiers, cleaning machines, skimmers, filters, lime and soda processes and zeolite softeners.

We will now consider the different methods of removing scale from boilers.

The first of these methods, whose only virtue lies in the fact that it is the oldest and in most general use, is the removal of scale by means of hammers, chisels, scrapers, etc. This laborious method is effective only in the older types of boiler, such as the two flue boiler. In the return tubular boiler the difficulties are multiplied by our inability to properly clean between the tubes. In the water tube boiler, this method is impossible.

The next method in common use is the boiler compound. Boiler compounds may be divided into the two classes, those which act chemically and those which act mechanically.

The chemistry of boiler compounds is correct and is thoroughly understood. One of those which act mechanically contains soap stone (magnesium silicate) which is supposed to give the surface of the boiler a gelatinous coating which will prevent the adherence of scale forming matter to the shell and tubes. Kerosene and crude oil are also used to penetrate the scale and loosen it from the tubes. The boiler compounds that act chemi-

cally are generally composed of soda in combination with some organic acid such as tannic, acetic, etc. The soda ash (sodium carbonate) forms the basis of nearly all such compounds.

Would rather buy "Blue Sky" than most boiler compounds on the market today, although some few boiler compounds would be better than nothing at all.

Another method of removing scale is by using "feed water heaters and purifiers."

One of the most common and familiar to most of you is the lime and soda process. I know that there are some before me now who are lime and soda advocates and I beg to differ with you as I consider you as belonging to the old school. Will state here that I am a strong advocate of the zeolite water softeners, except in some few cases where because of the nature of the raw water to be treated, lime and soda would be the better method of softening.

One reason for my being against lime and soda is that I have been in power plants where they were buying boiler compounds even after treating water with lime and soda. In other words boiler free scale will not result from treating water with lime and soda as a hardness of .3 or .4 is usually the lowest that can be obtained with this method.

Another objection to lime and soda is the close attention required by the operator as it is very easy to over or under treat the water, especially if the water tends to vary from time to time.

There are three main types of zeolite softeners, the Permutit, Borromite, and Refinite, the first being synthetic and the latter two, natural zeolites.

The Permutit was the original zeolite process. Dr. Robert Gans, a German, was the inventor, and the Permutit Company controls his patents

today in this country. He divided zeolites into three classes:

- (1) Alumina silicates.
- (2) Double silicates of alumina.
- (3) Crystalline zeolites with no exchange powers.

Synthetic exchange silicates may be produced by precipitation or fusing. In the latter felspar, kaolin, pearl ash and soda are fused together in definite proportions. The glass thus produced is crushed and is then lixurated to remove the soluble silicates. This residue constitutes the insoluble grains characteristic of exchange silicates. All slight residual alkalinity which may be remaining completely disappears after the first regeneration with a 10% salt solution so that water passing thru a layer of exchange silicates is not only near zero hardness but is also absolutely neutral in the presence of phenolphthalein. So much for the synthetic zeolite.

Borromite is finely granular reddish brown colored mineral dehydrated natural alumina ferro-silicate.

In Ardmore, South Dakota, there are five hundred acres of natural zeolite owned by the Refinite Company of Omaha. Their softener is operated on the same principal.

In summary consider the zeolite process the best for water softening because:

(1) Every water, however hard, can be reduced to zero hardness simply by being passed thru a layer of zeolite. No other process except distillation will accomplish this result.

(2) No chemicals are added to the water. The action is perfectly automatic.

Furthermore, the raw water may vary in composition while in the old systems of water softening, a chemist should be required to apportion the doses of chemicals necessary to prevent under-treatment (leaving excess

sive hardness) or over-treatment (having excessive causticity.)

No matter how efficient a steam power plant may be, or how carefully everything pertaining to its operation may be recorded, the vital factor in the economy of the entire steam plant is the efficiency obtained from the steam boilers. The steam boiler may be considered a heat engine for changing the potential energy of coal into the potential energy of steam. The steam engine is a machine for changing the energy of steam into mechanical work. The engineer does everything in his power to make the losses of this transfer a minimum by using every known device that can possibly increase the economy of his engine and yet the same engineer will allow to collect on the heating surface of the boiler a practically permanent, non-conducting, heat-absorbing, steam retarding scale that seriously reduces the efficiency of the entire steam plant. The first step toward maximum efficiency should be to secure a feed water that cannot possibly corrode or scale the boiler.

The writer recommended Borromite to his company because of its flexibility as with a quick regeneration any sudden demand for steam can be taken care of very easily.

The Borromite zeolite is a natural product mined in this country and is known as a natural zeolite sand. The sand is very carefully washed and passed through a highly refining process, which increases the exchange power of the mineral and at the same time developing a greater resistance in the grains. The Borromite zeolite is one of the oldest known zeolites, having been used for many purposes as long ago as 1860.

The mineral in chemical composition consists of iron aluminum silica with sodium in combination, the sodium ion being exchangeable for

other ions such as calcium and magnesium.

The Refinite mineral is mined at Ardmore, S. Dak., as a natural clay consisting of aluminum silicate. This mineral is fused with a sodium salt shredded in the form of noodles and ultimately baked at a high temperature.

Both the Permutit and Refinite zeolites are known as slow exchange silicates, meaning that the sodium exchange is carried on at a slow rate necessitating a uniform flow of water at a low rate passing through the bed to secure zero hardness. In reconditioning or salting following a capacity run, the slow acting zeolites require 8 to 12 hours time before complete regeneration. In contrast to the Permutit and Refinite materials, the Borromite zeolite is known as a rapid rate exchange silicate, meaning that the reaction is instantaneous and that water can pass through the Borromite bed at fluctuating rates of flow, giving the system greater flexibility in meeting peak demands for soft water.

Likewise, in reconditioning this rapid rate property permits regeneration in less than 30 minutes, permitting a greater flexibility in operation and assuring an adequate supply of soft water to meet any sudden demand for steam.

References: Journals of different water softening companies.

The Methods Committee

The Official Standard Methods have been revised and at present the committee is working on the proposed tentative methods for the various determinations used in the flour mill laboratories and in cereal work. These require considerable time as we are attempting to give actual working conditions under which the determinations are made, and are checking in our own laboratories the methods proposed.

The Committee.

ABSTRACTS

The following Abstracts taken from
Experiment Station Record.

The Editor.

THE VITAMIN CONTENT OF RICE BRAN, AND METHODS FOR ITS DETERMINATION, B. C. P. Jansen, *Meded. Geneesk. Lab. Weltevreden [Dutch East Indies]*, 3, ser. A. No. 1-3 (1920), pp. 22-49).—The author reviews the literature on the extraction of the antineuritic vitamin from rice bran by various solvents, and reports an investigation of the relative value of certain of these solvents as determined by feeding experiments with pigeons and domestic fowls, using the various extracts of rice bran as curative and protective agents in connection with a polished rice diet. Four methods of extraction were used, (1) with 0.3 per cent HCl for 2 days, (2) with 0.3 per cent HCl for 30 days, (3) with 70 per cent alcohol, and (4) with 96 per cent alcohol and $\frac{1}{15}$ volume of concentrated HCl. In each case 1 kg. of the rice bran was thoroughly shaken with 3 liters of the solvent, allowed to stand for some time, filtered, and the solution evaporated on a calculated quantity of washed white rice. The evaporation was conducted at a temperature not exceeding 50° C. and hastened by a current of air. The resulting materials contained the extracts from 5, 10 and 15 per cent of the rice bran, preliminary experiments having indicated 30 per cent to be more than sufficient.

In the feeding experiments with healthy cocks the 5 per cent rice bran proved sufficient to prevent polyneuritis with all the extracts except the fourth. With this, one of the three cocks developed polyneuritis. Of three controls fed white rice and 5 per cent of rice bran, two died of intercurrent diseases and the third of polyneuritis. This is thought to indi-

cate that 5 per cent of rice bran is the limit at which an attack of polyneuritis is possible, and that consequently all of the vitamin was extracted by the methods employed.

With pigeons, several developed polyneuritis on the 5 per cent extract but were protected with a 10 per cent extract. This indicated that pigeons are more susceptible to polyneuritis than fowls. Other experiments with pigeons were conducted in which the extract was prepared from another supply of bran which proved to contain considerably less vitamin. This is explained on the ground that the first supply was from freshly cut rice, while the other was from a stock that had been stored for some time. As the result of this experimental work the author recommends as the simplest method of obtaining the most potent preparation extracting with 0.3 per cent HCl, evaporating the extract to a sirup at low temperature, and quickly adding an equal volume of alcohol. A thick precipitate forms which is filtered off, leaving the vitamin in the filtrate.

The author is of the opinion that the best method as yet for determining antineuritic vitamin quantitatively is by feeding healthy fowls or pigeons with washed white rice mixed with the substance to be tested. Curative experiments with polyneuritic fowls are considered to be absolutely worthless. Two means of improving the methods in use are discussed, (1) the use of more susceptible subjects than pigeons and (2) the substitution of a more delicate criterion than the appearance of nerve degeneration. For the first the use is suggested of a species of small birds known as "nonnetjes" (*Munia maja*.) These birds are said to contract polyneuritis in less than 12 days. The small size of the birds, moreover, makes it possible to keep several in

the same cage and thus eliminate individual errors. A more detailed study of metabolic changes occurring in the development of polyneuritis is thought necessary before a more delicate criterion can be discovered than the characteristic nerve changes.

STUDIES IN THE VITAMIN CONTENT. W. H. Eddy and H. C. Stevenson (*oJur. Biol. Chem.*, 43 (1920), No. 1, pp. 295-309, fig. 1).—An investigation of Bachmann (E. S. R., 42, p. 59) and Williams (E. S. R. 41, p. 670) methods of determining water-soluble B has led to a modification of the latter method as follows:

The materials used in the test are capillary pipettes, a dilute suspension of yeast cells (Fleischmann) in Nagelis solution, and a sterile solution of the vitamin extract to be tested. A suspension of the yeast cells from an agar slant is made by shaking as small a portion as can be taken up on the point of a needle in 10 cc. of the Nagelis solution for 2 or 3 hours in a mechanical shaker. One unit of the yeast suspension and one unit of the vitamin extract are drawn up into the sterilized pipette and mixed, the ends of the pipette sealed, and the tubes incubated for 20 hours at 35° C. The tips of each pipette are then broken, a bulb is placed on the large end, and the contents blown out on a slide, fixed and stained. For control, another series of pipettes is prepared and filled by drawing up a unit of yeast suspension without the unit of vitamin. These are incubated and counted in the same way as the test pipettes. By using a number of tubes for each test greater accuracy can be secured.

The results are reported of various applications of the method. Trial tests have indicated that the test is sensitive to small amounts of vitamin extract. The specificity of the test is shown by the results obtained with small quantities of the Funk antineu-

ritic vitamin. Tests with navy bean extract and with sterile orange juice, before and after extraction with Lloyd's reagent, indicate the selective adsorption of the active constituent by the reagent and further prove the specificity of the test for B-vitamin. That the stimulus removed in the case of the orange juice was the B-vitamin and not the C was further proved by positive results obtained in prophylactic and curative experiments with guinea pigs, using as the active reagent the filtrate from the Lloyd reagent extract which had failed to cause increase in yeast cells.

Other tests reported indicate that at 120° a partial destruction of the vitamin takes place, and that alkalis also have a destructive effect. Estimations of the content of this vitamin in the jugular and mammary vein plasma of a pregnant cow showed the mammary vein to contain appreciable amounts.

Comparative estimations of the B-vitamin content of different food-stuffs were made by the following method: "First, establish by counting of units the probable range of variation in the suspension used. Second, make from 5 to 10 tests on each substance tested, and in these tests eliminate all zero readings as showing that the unit in that case contained no cells. Average all other readings. Repeat as often as seems necessary to clear up doubtful positions."

The results are given of this procedure as applied to extracts of different materials prepared by drying the material at 60°, extracting equivalent amounts for the same length of time in boiling water, making up to the same volume, and sterilizing in the Arnold sterilizer. The results of five determinations on each extract are reported. The substances tested in decreasing order of potency were alfalfa, potato, celery, apple, tomato, cucumber, turnip, radish, onion, and

carrot. While these results are not considered conclusive, it is pointed out that in certain cases they harmonize with the feeding results recently obtained by Osborne and Mendel (E. S. R. 42 p. 759.)

SOME FACTORS RELATED TO THE QUALITY OF WHEAT AND STRENGTH OF FLOUR. W. L. Stockham (*North Dakota Sta. Bul. 139* (1920), pp. 69, figs. 16.).—A large amount of experimental work of the station is summarized, with frequent citations from the work of other investigators, furnishing as a whole a comprehensive discussion of the factors which determine quality in wheat and strength of flour.

"The strength of a flour is its apparent and potential ability to make a large good textured loaf, that of a wheat its production of strong flour, and of a variety the general average rank of flour from it as compared to other varieties grown under the same conditions. The strength of a class of wheat is the rank of its flour compared to that of other classes when each are grown under the conditions for which they are adapted. Strength is limited largely by varietal inheritance and climate.

"Hard red spring wheat ranks first in strength, followed in order by hard red winter, durum, soft red winter, and soft white winter.

"The best grades of flour from any class are those from the reduction of purified middlings and free from particles not natural to the endosperm of the wheat.

"Within any variety smallness in size of kernels usually indicates greater relative strength. The extremely small kernels, however, are sometimes very weak. Size is of little importance in comparing classes or varieties. The hard spring and winter classes, which rank highest in strength, average smaller than the softer classes."

"External color of wheat is not closely related to strength.

"The hard vitreous kernels are the stronger except in the extremely hard and badly shrunken material.

"Bright samples of wheat are relatively more free from bacteria and molds than those which are bleached or damaged. A badly-frosted sample was free from bacteria and molds.

"The softer the wheat and lower the grade of flour the less granular the flour. Damage changes the flour texture.

"The composition of the kernels is influenced somewhat by the soil but more largely by the moisture conditions. The best conditions for growth produce a lower protein content and larger yield per acre but wheat lower in strength than that where conditions are not favorable because of insufficient or excessive moisture.

"The natural soil nitrogen in the drier regions is higher where that in the wheat is low. The opposite is true in the more humid sections. Nitrogen applications may increase the nitrogen content and strength of wheat. Wheats from the plats continuously planted to wheat did not differ materially in strength from those from the rotation plats.

"In all classes of wheat the nitrogen percentage gradually increases from the interior of the kernel to the outer layers except in the bran, where it again decreases. The grade of flour having the lower nitrogen content is likely to be stronger than those of higher nitrogen content from the same wheat. The outer layers are weakening.

"Added gluten increases the volume of the loaf. On the average with all grades of flour, the higher the percentage of protein the greater the strength to a certain point. Beyond this in the harder classes there are indications of weakness. Protein from hard red spring and hard red winter wheat because of its physical condi-

tion and surroundings is more efficient, i. e., flours of these classes are stronger than those of the soft winter and durum of the same protein content considering the prevailing varieties grown.

"The lower grades of flour generate gas at a more rapid rate during fermentation than the higher, and their weakness therefore must be attributed to other causes. Lack of gas generation is the limiting factor in strength in some cases, but one which may be overcome artificially. The quantity of water extracts is related to the gas penetrating power of a flour, but does not parallel strength because of the high percentage of extractives in low-grade flour. Bin-burned wheat flours are not usually high in extractive.

"The common inseparable impurities of wheat were not high in extractives except vetch, which sometimes stimulates fermentation in flours containing a low proportion of it.

"The ether extract of wheat is a decided improver of baking quality and strength, differing in this regard from other fats tried and the fatty acids.

"The percentage of total nitrogen of a straight flour soluble in a 5 per cent potassium sulphate solution is a less valuable index of strength than the total nitrogen figure.

"Amylolytic enzymes contribute to fermentation and large loaf volume. Proteolytic enzymes of wheat tend to weaken the gluten. The scutellum of the germ is the chief source of the enzymes. The higher grades of flour are more free from them than the lower. . . . Proteolytic activity gradually decreases in flours in storage. Sprouted wheat flours retain their activity in storage for a few years. The gluten is an aid and possibly an essential to an increase of the enzyme which destroys it.

"The proteolytic activity of wheat is greater than that of the flour from

it. The more active samples usually produce a flour requiring a shorter fermentation period in the pan. Flours of the same grade are not strong or weak according to their proteolytic activity. High proteolytic and high amylolytic activity are usually associated.

"Weathering increases and distributes the enzymes of wheat. Bin-burned wheat was still active proteolytically.

"Flours of the same protein content from different classes of wheat differ in average absorption. There is the same deficiency of the soft red winter. Durum protein ranks highest. The strength limits of any class of wheat are better measured by absorption protein ratio than by the percentage of crude protein.

"Although the percentage of ash runs up with protein content, a higher portion of the water would function in overcoming stiffness and would be more available for fermentation.

"Too high temperature during fermentation for baking produces an irreparable damage.

"The quantity of ash of wheat bears the same general relation to strength of the wheat as that of the flour from it. Hard red spring wheats high in ash yield flours high in ash and relatively strong in most cases.

"The quantity of moisture sufficient to prevent gluten recovery from a flour is closely related to the amount necessary for gluten reactions at the time of kernel formation. The tendency for gluten particles to cohere depends upon the amount of available moisture and the severity of mechanical treatment.

"The weaker acids are dispersive to gluten over greater range than the strong, and the concentrations necessary to overcome their own dispersive effects are greater. The relative conductance of a normal solution of va-

rious acids ranks them fairly well as to the critical concentrations for overcoming dispersion.

"Dispersion of gluten is also produced by some organic salts and a tendency toward dispersion by antecedent and cleavage products of gluten. The fatty acids and acids of wheat fat do not produce dispersion. The ability of salts to overcome dispersion is determined by the valence product of the salts primarily, salts of heavy metals being relatively more efficient, however, than salts of equal valence and less mass.

"Normal salts in low concentration do not greatly affect the baking strength of strong flour. The period of maximum gas formation is not changed greatly by their addition though some stimulating action results. Uni-univalent salts are less harmful as a rule than those of higher valency type. Most of the acid salts except those of phosphoric and the weak organic acids are disastrous to strength. Strong flours may stand more acid than the weak. In fact, they may occasionally be improved thereby.

"Acids adversely change the shape much more than salts and alkalis in equivalent concentrations. Salts influence the absorption of starch similarly to that of gluten. Starch gives lower figures with alkalis, and with mineral acids lower than organic when treated as dough. Dehydration reduces absorptive capacity of starch, and hydration increases it.

"Starch is continually undergoing change as is gluten. Starch is more permeable than gluten. Salt and acids produce increases in permeability, and mixtures of the two are very active in this respect.

"The conditions within which leekthin has its colloidal properties modified are similar to those for the modification of gluten.

"A flour increases in strength in storage under good conditions for a

few months, remains fairly constant for a time, and deteriorates after a period of approximately two years. Flour from wheat nine years old deteriorates in four months. The rate of deterioration of flour is about four times as fast as with a wheat under the same conditions.

"Salts of a higher valency interfere less with vital phenomena than those of low valency and are relatively less active in the presence of colloidal material because of their precipitating effects. Though salts in dilute stimulating concentrations increase the rate of vital changes, they may not increase the total amount of material converted.

"The germ is the chief source of oxidizing enzymes. They have little bearing on strength but are responsible or related to some color reactions of bran and low-grade flours."

CHANGES TAKING PLACE IN THE TEMPERING OF WHEAT. E. L. Tague, (*Jour. Agr. Research* [U. S.], 20 (1920), No. 4, pp. 271-275.—With a view to standardizing time, temperature, and moisture conditions for the tempering of wheat before grinding to flour, tests were conducted at the Kansas Experiment Station on three lots of wheat, a variety of hard wheat known as Kanred, developed at the station, a hard red wheat from central Kansas, and a soft wheat from Colorado, known as Arizona White. The conditions tested were a time of 24, 48, and 72 hours, temperatures of 5, 20, and 40° C., and a moisture content of 15.5 and 18 per cent. The original moisture content of the wheat, as determined by drying in the air oven at 110° to constant weight, was found to be 12.65 per cent for Kanred, 10.86 for hard red winter wheat, and 10.8 for the Arizona White.

A 200 gm. sample of the wheat was weighed out into a 500 cc. bottle and brought up to the desired moisture

content by the addition of distilled water. The bottle was then corked, shaken, and placed in a large water thermostat which had been brought to the desired temperature. After remaining the specified time the bottle was removed and the wheat ground as rapidly as possible in a flour mill, each sample being put through the mill the same number of times. The milling qualities of the wheat were noted and the yields or straight flour were calculated, after which the flour was analyzed for H-ion concentration, total acidity, water soluble phosphorus, and titrable nitrogen by the methods previously described by Swanson and Tague (E. S. R., 40, p. 507). For each variety of wheat an untempered sample was ground and analyzed in the same way.

The milling qualities of all the wheats were improved by tempering to a moisture content of 15.5 per cent. A moisture content of 18 per cent proved too high, the resulting flour being sticky and tending to clog the sieves. The milling qualities of the drier and hard wheats were improved by tempering more than the wetter and soft wheat. At 5° practically no chemical changes of the wheat occurred, while at 20° an increase in H-ion concentration, total acidity, water soluble phosphorus, and titrable nitrogen occurred. These changes were even more pronounced at 40°. The time of tempering appeared to be a factor in chemical changes, but not in physical. Both yield and milling quality were the best at a temperature of 20 to 25°, the physical changes at 40° proving detrimental to the milling qualities.

BREAD MAKING IN PANS OF DIFFERENT MATERIALS. F. A. Osborn, (*Jour. Home Econ.*, 11, (1919), No. 8, p. 352.)—This paper records the results of baking tests, under regulated conditions, with bread pans of different materials, including graniteware,

Russia iron, tin, pyrex, unpolished aluminum, and polished aluminum. burning was found in the granite pans, with the others following in the order given. The bread in the polished aluminum pan was a light brown, and not burned at all.

THE DISTRIBUTION OF ENZYMES AND PROTEINS IN THE ENDOSPERM OF THE WHEAT BERRY. F. J. Martin (*Jour. Soc. Chem. Indus.*, 39 (1920), No. 23, pp. 327T.-328T.).—A study is reported of the nature and extent of the variations in flour from different parts of the wheat berry with respect to enzymic activity and quantity and quality of flour. A single wheat, Barusso Plate, was milled for this experiment, and four samples of reduction flour from different parts of the grain, two of break flours, and one of straight grade flour representing the entire endosperm were used. The enzymic activity was measured by the amount of gas the flour was capable of producing in 24 hours when fermented with a given amount of yeast. Gluten was determined wet and dry after washing out the starch. The gas-retaining capacity of the gluten was determined by measuring the volume of doughs contained identical amounts of gluten from the different sources. Confirmatory baking tests with the different sources. Confirmatory baking tests with the different flours were also made. The results obtained are summarized as follows:

“The enzymic activity, as shown by the evolution of carbon dioxide on fermentation, increases progressively from the interior to the exterior of the endosperm. The quantity of gluten increases in the same manner. The quality of the gluten varies considerably, being good in flour from the interior of the endosperm and deteriorating progressively in flour from regions approaching the cortex. The effect of the combination of the increasing quantity with decreasing

quality of gluten tends to produce flours of a common 'strength' from various parts of the wheat berry.'"

AN EXPERIMENTAL STUDY OF THE EFFECT OF CERTAIN ORGANIC AND INORGANIC SUBSTANCES ON THE BREAD-MAKING PROPERTIES OF FLOUR AND ON THE FERMENTATION OF YEAST. H. Masters and H. Maughan (*Uiochem. Jour.*, 14, (1920), No. 5, pp. 586-602)

—The authors have investigated the effect of certain organic and inorganic substances on the bread-making properties of flour. The samples of flour represented, in addition to wheat flour of 80 per cent extraction, the various combinations of wheat flour of from 75 to 90 per cent extraction with barley, rice, maize and rye flours which were used in England during the war. The baking experiments included studies of the effect of the addition of lime water, of alternate reduction and increase in the atmospheric pressure on the expansion of the gluten and of the addition of ox serum, phosphates, and potato alone or combined. Measurements were also made of the amount of fermentation produced by yeast with the various ingredients in the absence of flour and also of the expansion of the dough prior to baking.

The addition of lime water, while neutralizing any acidity in the flour, did not prevent the production of acid and tended to decrease the size of the loaf. It was found impossible to alter the final size of the loaf by stretching the dough through alternate increase and decrease in pressure in a vacuum desiccator.

Fresh ox serum added in 1 per cent concentration caused a marked increase in the volume of the loaf. This property of the serum was found to diminish rapidly on keeping, but was not destroyed by heating to from 50 to 60° C. Gelatin, egg, and blood albumin, caseinogen and lime water, and gelatin alone did not prove

satisfactory as substitutes for ox serum. The addition of phosphates tended to increase the size of the loaf, the maximum increase occurring on the addition of 1 part of monosodium dihydrogen phosphate to 200 parts of the flour. Neither phosphate nor serum produced any increase in the size of the loaf when the bread was raised with chemical raising agents.

In the baking tests with varying proportions of potato, cooked and raw, the best results as to size, texture, etc., were obtained with a mixture containing boiled potato equivalent to from 25 to 33 per cent of the total weight.

The experiments on fermentation of the yeast with the various ingredients whose effect on the properties of the bread was studied in the first part of this investigation and measurements of dough expansion were in general in agreement with the baking experiments, an exception being the results obtained with potato. Raw potato stimulated the action of the yeast to a greater extent than boiled potato, but a larger loaf was obtained with the boiled potato than with the raw.

THE HUMPHRIES PROCESS

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the wheat has approx. 1% of H_2O added by this process, the final flour shows an increase of only approx. 0.2% moisture. It is assumed therefore that the H_2O added is absorbed by the proteins to form a colloidal mass from which the H_2O cannot be removed by physical methods. The H_2O mols. are absorbed by the proteins and starch by virtue of their surface energy. There are thus 2 opposing forces, that of the surface energy of the flour particles absorbing the H_2O and that of the H_2O attracting itself and acting in opposition to the first force. Therefore if H_2O is brought in contact with this system

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THE HUMPHRIES PROCESS

(Cont. from Page 43.)

(Humphries process) the equil. is displaced in the direction of the absorptive surface energy of the flour. As a result H_2O is taken up and the flour changes its physical properties. Advantage is taken of the fact that certain acids, acid salts and nitrates accelerate the swelling of the proteins, whereas chlorides, phosphates, sulfates, citrates, tartrates, $EtOH$ su-

gar, dextrin and certain gums retard this action. By the Humphries process mixts. of 40% wheat poor in gluten and 60% wheat with soft, poor gluten were treated with 0.2-0.3 per cent of $(NH_4)_2HPO_4$, Na^2HPO_4 , $CaHPO_4$, $(NH_4)_2SO_4$ or Na^2SO_4 . The final baked products were much superior in appearance, finer grained and more elastic than without the salt addition. The increase in vol. was 8-14%.

C. C. Davis.

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